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Electronic Supplementary Information

Stereoselective synthesis of amino-substituted cyclopentafullerenes promoted by magnesium perchlorate/ferric perchlorate

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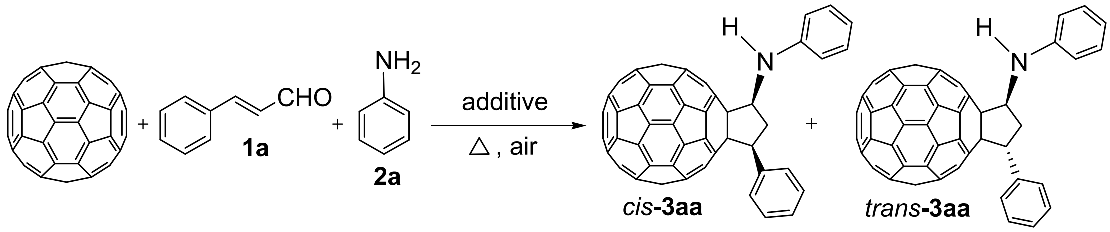
Optimization of reaction conditions for arylamines/secondary amines

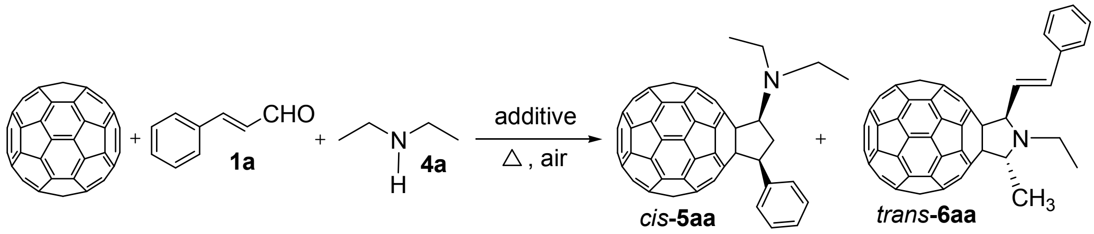
Table S1 Optimization of reaction conditions for the reaction of C_{60} with cinnamaldehyde **1a** and aniline **2a**[a]



Entry	Additive	Molar ratio[b]	Temp. (°C)	Time (min)	Yield (%) of *cis*-**3aa**[c]	Yield (%) of *trans*-**3aa**[c]
1	$Mg(ClO_4)_2$	1:5:5:1	180	120	15 (68)	6 (27)
2	$Mg(ClO_4)_2$	1:10:10:1	180	60	16 (52)	13 (42)
3	$Mg(ClO_4)_2$	1:20:20:1	180	40	12 (50)	11 (46)
4	$Mg(ClO_4)_2$	1:10:10:3	180	30	22 (54)	18 (44)
5	**$Mg(ClO_4)_2$**	**1:10:10:4**	**180**	**60**	**33 (75)**	**10 (23)**
6	$Mg(ClO_4)_2$	1:10:10:5	180	40	26 (74)	8 (23)
7	$Mg(ClO_4)_2$	1:15:10:4	180	40	27 (59)	16 (35)
8	$Mg(ClO_4)_2$	1:5:10:4	180	120	2 (20)	trace
9	$Mg(ClO_4)_2$	1:10:15:4	180	30	22 (56)	15 (38)
10	$Mg(ClO_4)_2$	1:10:5:4	180	60	11 (61)	4 (22)
11	$Mg(ClO_4)_2$	1:10:10:4	160	70	20 (67)	9 (30)
12[d]	$Mg(ClO_4)_2$	1:10:10:4	180	90	32 (78)	8 (20)
13	$AlCl_3$	1:10:10:4	180	60	8 (36)	3 (14)
14	$Fe(ClO_4)_3{\cdot}xH_2O$	1:10:10:4	180	90	0	0
15	$Mn(OAc)_3{\cdot}2H_2O$	1:10:10:4	180	150	0	0
16	$CuCl_2$	1:10:10:4	180	120	0	0
17	$Cu(OAc)_2$	1:10:10:4	180	120	0	0

[a]Unless otherwise indicated, all reactions were performed in *o*-dichlorobenzene (ODCB) under air conditions. [b]Molar ratio refers to C_{60}/**1a**/**2a**/additive. [c]Isolated yield; those in parentheses were based on consumed C_{60}. [d]The reaction was conducted under nitrogen atmosphere.

Table S2 Optimization of reaction conditions for the reaction of C_{60} with cinnamaldehyde **1a** and diethylamine **4a**[a]



Entry	Additive	Molar ratio[b]	Temp. (°C)	Time (min)	Yield (%) of *cis*-**5aa**[c]	Yield (%) of *trans*-**6aa**[c]
1	$Mg(ClO_4)_2$	1:10:10:4:0	100	90	18 (58)	12 (39)
2	$Mg(ClO_4)_2$	1:10:10:2:0	100	90	29 (55)	22 (42)
3	$Mg(ClO_4)_2$	1:10:10:1:0	100	90	36 (55)	25 (38)
4	$Mg(ClO_4)_2$	1:10:10:0.5:0	100	60	37 (63)	20 (34)
5	$Mg(ClO_4)_2$	1:10:10:0.2:0	100	60	18 (40)	26 (58)
6	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:10:0.5:0.5	100	50	28 (53)	14 (26)
7	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:15:0.5:0.5	100	50	40 (59)	17 (25)
8	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.5	100	35	40 (70)	7 (12)
9	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:25:0.5:0.5	100	30	38 (72)	7 (13)
10	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:5:20:0.5:0.5	100	35	35 (81)	6 (14)
11	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:15:20:0.5:0.5	100	15	31 (45)	18 (26)
12	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.2	100	20	32 (41)	12 (15)
13	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:1	100	40	40 (69)	9 (16)
14	**$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$**	**1:10:20:0.5:0.5**	**80**	**60**	**40 (80)**	**8 (16)**
15	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.5	60	110	15 (79)	trace
16[d]	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.5	80	60	39 (78)	8 (16)
17	$Mg(ClO_4)_2$	1:10:20:0.5:0	80	40	25 (76)	4 (12)
18	$Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0:0.5	80	60	29 (35)	21 (25)
19	$Mg(ClO_4)_2/CuCl_2$	1:10:20:0.5:0.5	80	60	18 (50)	10 (28)
20	$Mg(ClO_4)_2/CuCl_2{\cdot}H_2O$	1:10:20:0.5:0.5	80	45	20 (65)	8 (26)
21	$Mg(ClO_4)_2$/DMAP	1:10:20:0.5:0.5	80	70	30 (51)	11 (19)
22[e]	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.5	80	60	39 (80)	5 (10)
23[f]	$Mg(ClO_4)_2/Fe(ClO_4)_3{\cdot}xH_2O$	1:10:20:0.5:0.5	80	60	22 (71)	6 (19)

[a]Unless otherwise indicated, all reactions were performed in chlorobenzene under air conditions. [b]Molar ratio refers to C_{60}/**1a**/**4a**/$Mg(ClO_4)_2$/other additive. [c]Isolated yield; those in parentheses were based on consumed C_{60}. [d]The reaction was conducted under nitrogen atmosphere. [e]The reaction was carried out in *o*-dichlorobenzene (10 mL).

[f]The reaction was conducted in toluene (10 mL).

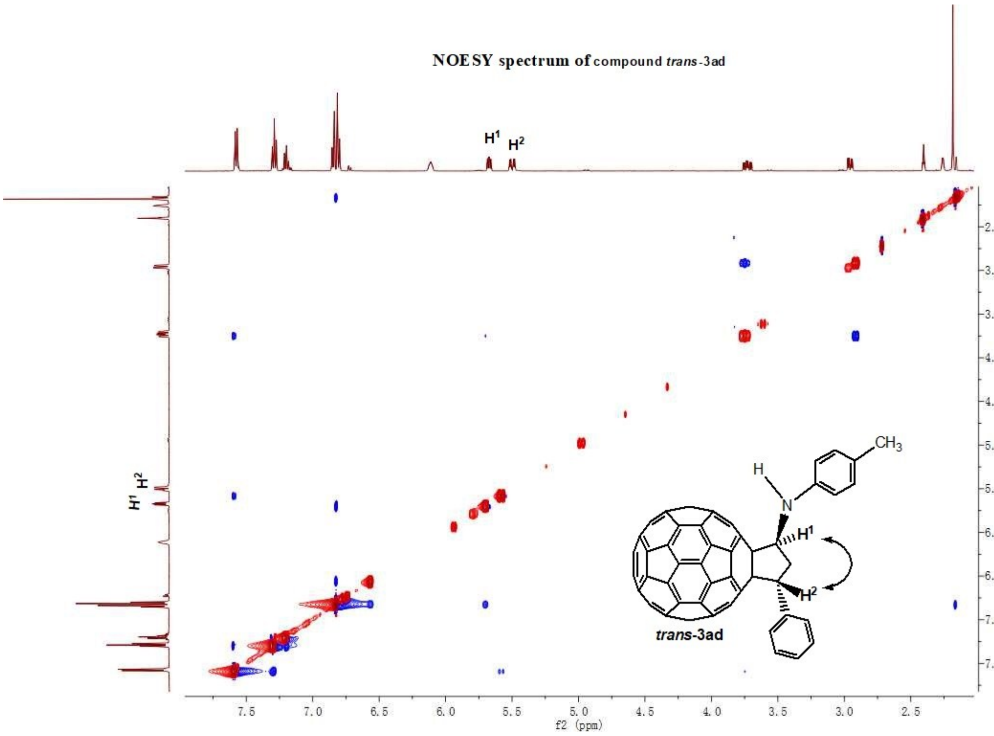


Figure S1. NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *trans*-**3ad**.

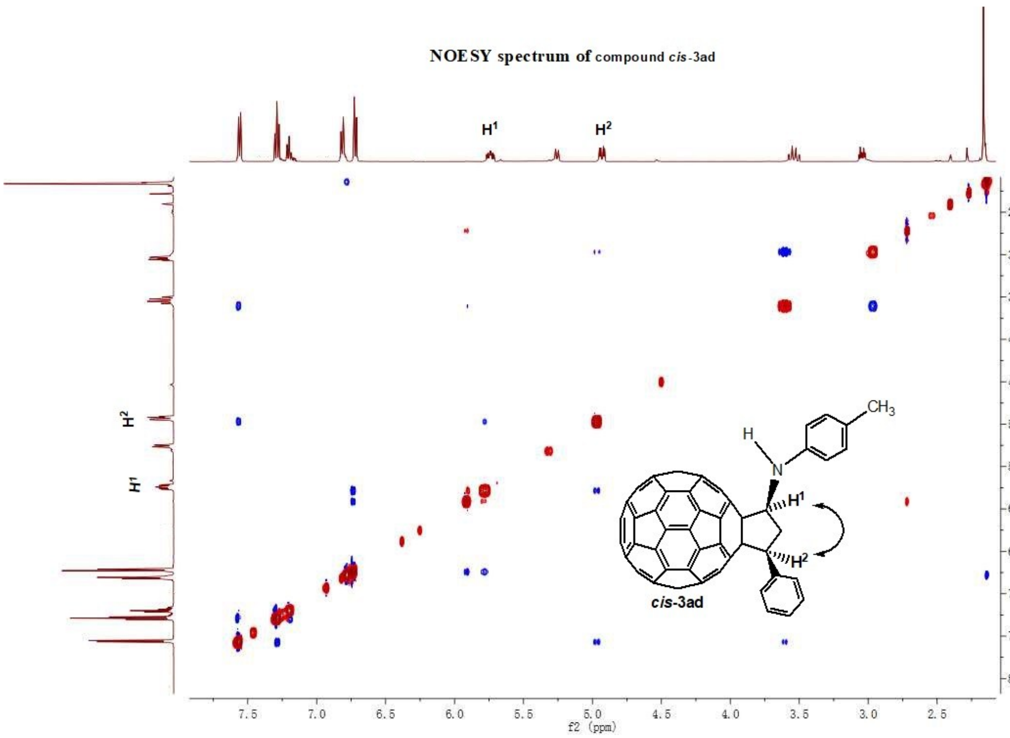


Figure S2. NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *cis*-**3ad**, and the nuclear Overhauser effect between the two methine protons is indicated by the curved arrow.

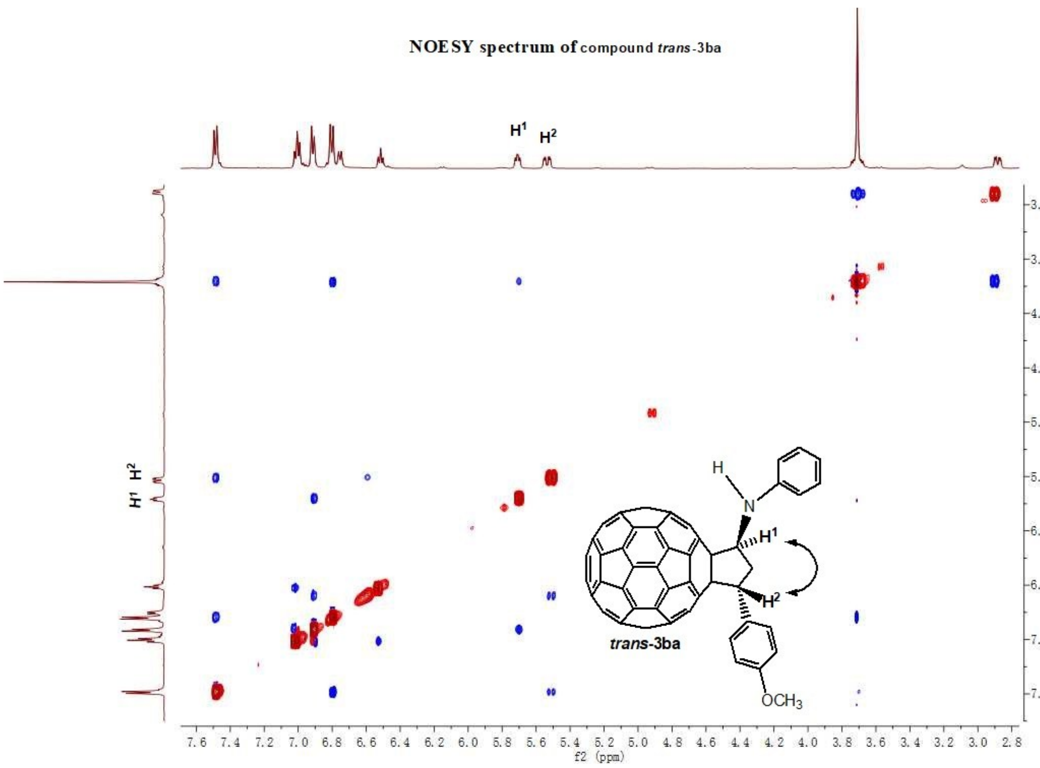


Figure S3. NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *trans*-**3ba**.

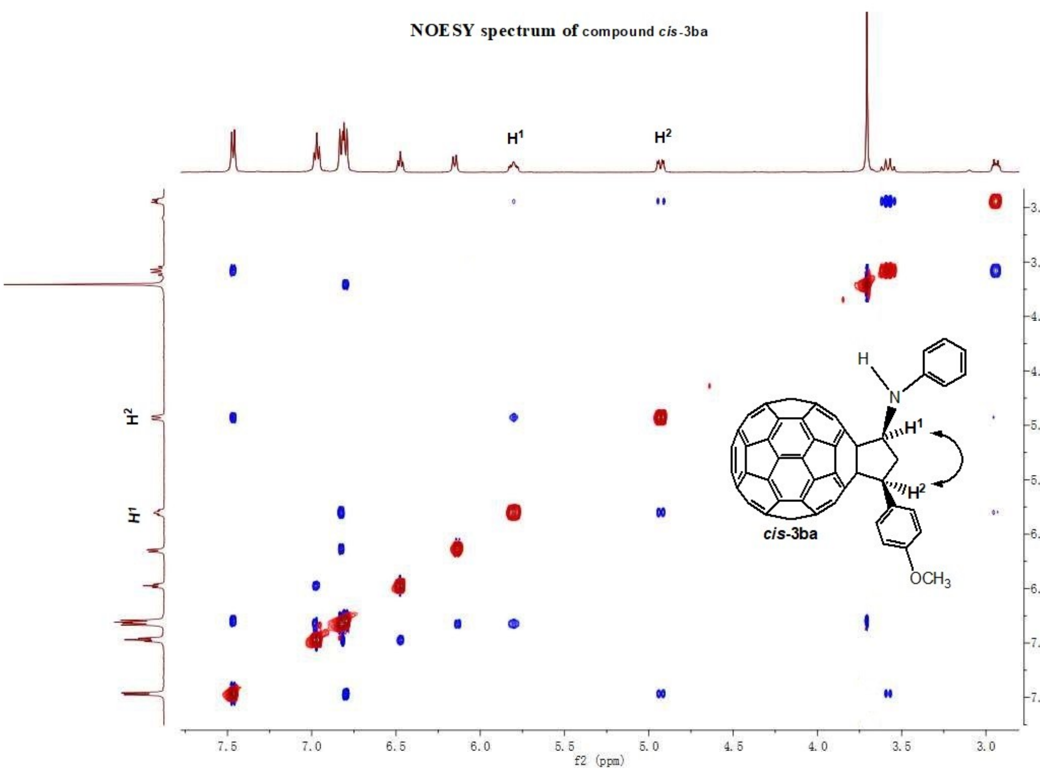
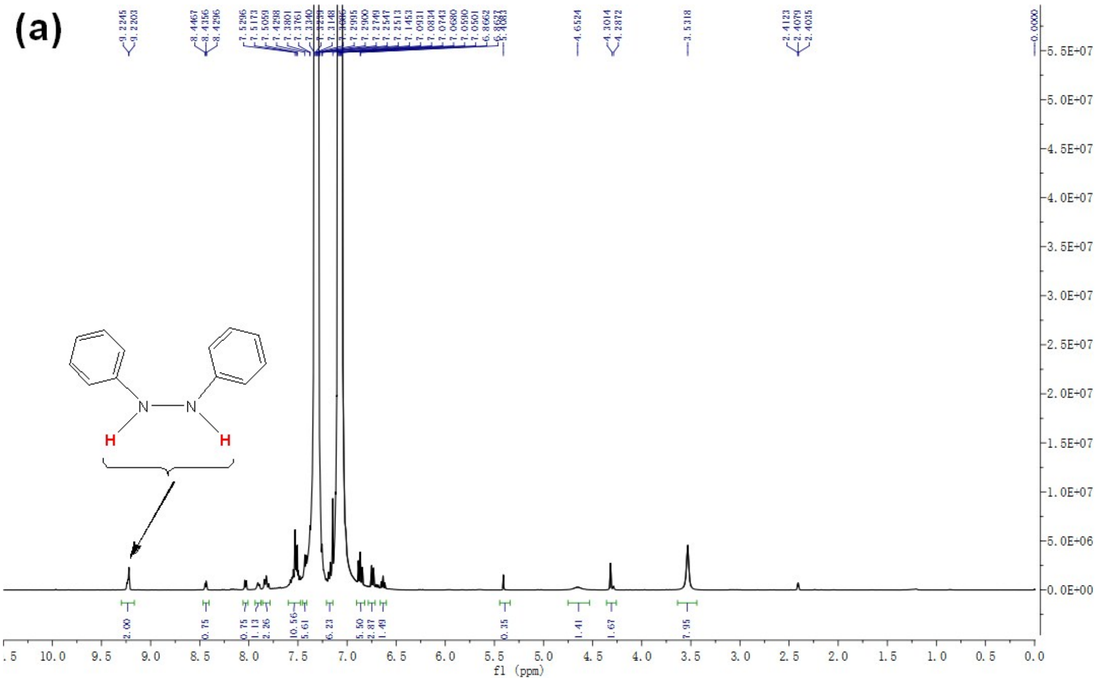


Figure S4. NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *cis*-**3ba**, and the nuclear Overhauser effect between the two methine protons is indicated by the curved arrow.



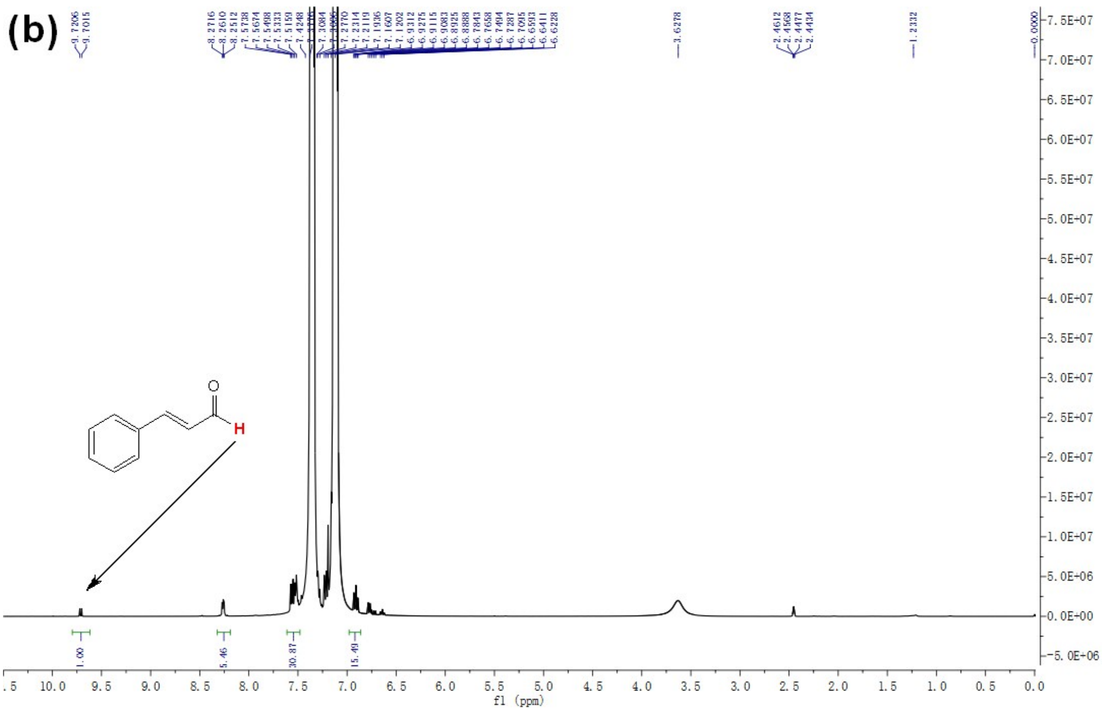


Figure S5. (a) ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of the reaction mixture of C_{60}, cinnamaldehyde (**1a**), aniline (**2a**), and $Mg(ClO_4)_2$ for 1 h under the optimized conditions. (b) ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of the reaction mixture of C_{60}, cinnamaldehyde (**1a**), aniline (**2a**), and $Mg(ClO_4)_2$ for 0 h under the optimized conditions.

Experimental details and spectra data

General procedure for the synthesis of amino-substituted cyclopentafullerenes 3. C_{60} (36.0 mg, 0.05 mmol), cinnamaldehydes **1** (0.50 mmol), arylamines **2** (0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) were added to a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. After they were completely dissolved in 6 mL of *o*-dichlorobenzene by sonication, the resulting solution was put into an oil bath preset at 180 ^{o}C and stirred under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60} and then amino-substituted cyclopentafullerenes **3**.

Cyclopentafullerenes *trans*-3aa and *cis*-3aa: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2a** (46 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 60 min afforded first unreacted C_{60} (20.1 mg, 56%) and then *trans*-**3aa** (4.7 mg, 10%, R_f = 0.68), *cis*-**3aa** (15.2 mg, 33%, R_f = 0.59) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *trans*-**3aa**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.59 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.9 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.5 Hz, 1H), 6.52 (t, J = 7.2 Hz, 1H), 5.73 (dd, J = 8.0, 5.3 Hz, 1H), 5.59 (dd, J = 14.4, 4.5 Hz, 1H), 3.80-3.73 (m, 1H), 2.92 (dd,

J = 12.7, 4.5 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.97, 154.26, 152.57, 152.53, 145.71, 145.60, 145.22 (2C), 145.08, 144.62, 144.30, 144.24, 144.22, 144.16, 144.09, 144.01 (2C), 143.98, 143.74, 143.61, 143.45, 143.37 (2C), 143.28 (5C), 143.10, 142.69, 142.55 (2C), 142.49, 141.12, 141.05, 140.75, 140.60, 140.52 (2C), 140.43, 140.28, 140.25, 140.23, 140.17, 140.10, 139.98 (3C), 139.80, 139.72, 139.63, 138.37, 137.68, 137.52, 137.45, 136.74, 135.81, 134.41, 134.14, 133.25, 127.79 (2C, aryl *C*), 127.56 (2C, aryl *C*), 127.04 (2C, aryl *C*), 126.10 (aryl *C*), 115.87 (aryl *C*), 111.84 (2C, aryl *C*), 76.15 (sp^3-*C* of C_{60}), 73.40 (sp^3-*C* of C_{60}), 63.50, 55.37, 35.15; FT-IR *ν*/cm^{-1} (KBr) 3395, 3042, 1599, 1498, 1456, 1426, 1313, 1251, 1183, 1152, 1077, 869, 783, 746, 694, 599, 570, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 310, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{15}N$ 929.1205; Found 929.1183. *cis*-**3aa**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.57 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.00-6.96 (m, 2H), 6.83 (d, J = 7.7 Hz, 2H), 6.49 (t, J = 7.3 Hz, 1H), 6.05 (dd, J = 9.8, 3.5 Hz, 1H), 5.84-5.79 (m, 1H), 4.98 (dd, J = 13.9, 4.4 Hz, 1H), 3.67-3.59 (m, 1H), 3.01-2.97 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.76, 153.09, 152.94, 152.54, 145.85, 145.79, 145.55, 145.06 (2C), 145.04, 144.18, 144.09, 144.07, 143.97, 143.95, 143.91, 143.86 (3C), 143.66, 143.56, 143.30, 143.19, 143.16, 143.10, 142.99 (2C), 142.96 (2C), 142.55, 142.35, 142.29 (2C), 140.94, 140.84, 140.52, 140.48 (2C), 140.41 (2C), 140.22 (2C), 140.11, 140.00, 139.86, 139.84, 139.75, 139.63, 139.60 (2C), 139.38, 137.72, 137.53 (2C), 137.08, 135.68, 134.33, 134.22, 133.56, 132.62, 127.50 (4C, aryl *C*), 127.09 (2C, aryl *C*), 126.05 (aryl *C*), 115.58 (aryl *C*), 111.90 (2C, aryl *C*), 74.07 (sp^3-*C* of C_{60}), 73.84 (sp^3-*C* of C_{60}), 64.54, 54.35, 34.58; FT-IR *ν*/cm^{-1} (KBr) 3399, 3028, 2881, 1599, 1500, 1456, 1428, 1317, 1252, 1226, 1185, 1150, 1070, 1015, 746, 693, 664, 571, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 311, 430; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{75}H_{15}N$ 929.1205; Found 929.1202.

Cyclopentafullerenes *trans*-3ab and ***cis*-3ab:** According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2b** (61.6 mg, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 40 min afforded first unreacted C_{60} (21.4 mg, 59%) and then *trans*-**3ab** (6.7 mg, 14%, R_f = 0.68), *cis*-**3ab** (10.5 mg, 22%, R_f = 0.59) as amorphous brown solid with CS_2/CH_2Cl_2 as eluent (V/V = 10/1): mp > 300 °C. *trans*-**3ab**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.58 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 6.9 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 2H), 6.35 (d, J = 8.0 Hz, 1H), 5.65 (dd, J = 7.8, 5.7 Hz, 1H), 5.57 (dd, J = 14.3, 4.4 Hz, 1H), 3.76-3.70 (m, 1H), 3.62 (s, 3H), 2.94-2.90 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.96, 154.19, 152.60, 152.50, 149.97, 145.45, 145.11 (2C), 145.02, 144.54, 144.18, 144.12 (2C), 144.04, 143.98, 143.91 (2C), 143.86, 143.63, 143.51, 143.39, 143.27, 143.25, 143.18 (2C), 143.16, 143.14 (2C), 143.00, 142.58, 142.47, 142.45, 142.38, 141.00, 140.96, 140.66, 140.49, 140.42 (2C), 140.32, 140.19, 140.14, 140.12, 140.07, 139.99, 139.88 (2C), 139.84, 139.69, 139.62 (2C), 139.53, 138.26, 137.57, 137.41, 137.36, 136.65, 135.63, 134.34, 134.02, 133.08, 127.69 (2C, aryl *C*), 126.93 (2C, aryl *C*), 125.98 (aryl *C*), 113.05 (2C, aryl *C*), 113.03 (2C, aryl *C*), 75.96 (sp^3-*C* of C_{60}), 73.30 (sp^3-*C* of C_{60}), 64.34, 55.20, 53.89, 35.01; FT-IR *ν*/cm^{-1} (KBr) 3419, 3119, 3026, 2929, 1510, 1384, 1367, 1239, 1182, 1098, 1034, 821, 756, 697, 660, 570, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}NO$ 959.1310; Found 959.1298. *cis*-**3ab**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.57 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 6.57 (d, J = 8.6 Hz, 2H), 5.77-5.70 (m, 2H), 4.96 (dd, J = 13.8, 4.1 Hz, 1H), 3.61 (s, 3H), 3.58-3.55 (m, 1H), 2.99-2.97 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.07 (aryl *C*), 153.36, 153.21, 152.77, 150.01, 146.20, 145.85, 145.33, 145.29, 145.26, 144.42, 144.33, 144.30, 144.23, 144.16, 144.15, 144.09 (3C), 143.91, 143.79, 143.53, 143.43, 143.40, 143.33, 143.25, 143.22, 143.19 (2C), 142.79, 142.60, 142.53 (2C), 141.18, 141.08, 140.76, 140.72 (2C), 140.65 (2C), 140.47 (2C), 140.36, 140.24, 140.08 (3C), 139.99, 139.86 (2C), 139.82, 139.61, 137.97, 137.73, 137.70, 137.32, 135.93, 134.60, 134.46, 133.79, 132.81 (aryl *C*), 127.73 (2C, aryl *C*), 127.24 (2C, aryl *C*), 126.20 (aryl *C*), 113.38 (2C, aryl *C*), 113.27 (2C, aryl *C*), 74.32 (sp^3-*C* of C_{60}), 74.09 (sp^3-*C* of C_{60}), 65.85, 54.60, 54.02, 34.93; FT-IR ν/cm^{-1} (KBr) 3364, 3028, 2942, 2890, 2825, 1602, 1510, 1457, 1428, 1357, 1288, 1237, 1181, 1146, 1099, 1069, 1037, 906, 819, 783, 762, 696, 664, 599, 571, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}NO$ 959.1310; Found 959.1281.

Cyclopentafullerenes *trans*/*cis*-3ac: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2c** (70 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 30 min afforded first unreacted C_{60} (29.8 mg, 83%) and then *trans*/*cis*-**3ac** (7.9 mg, 16%, *trans*/*cis* = 1/5.6, R_f = 0.66) as an amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**3ac**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.54 (d, J = 7.5 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 6.76 (s, 2H), 5.26-5.20 (m, 1H), 4.79 (dd, J = 13.7, 4.2 Hz, 1H), 3.65 (d, J = 12.2 Hz, 1H), 3.43 (q, J = 12.4 Hz, 1H), 2.92-2.88 (m, 1H), 2.42 (s, 6H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.46, 153.65, 152.49, 150.94, 146.47, 145.66, 145.25, 145.21, 144.83, 144.43, 144.31 (2C), 144.25 (2C), 144.14, 144.10, 144.02, 143.98, 143.86, 143.73, 143.68, 143.40, 143.34 (3C), 143.21, 143.14 (2C), 142.62, 142.59, 142.54, 142.48, 141.14, 141.09, 140.75, 140.70, 140.67, 140.60, 140.51, 140.45, 140.36, 140.24 (3C), 140.08, 140.03, 139.89, 139.81 (2C), 139.70 (2C), 137.99, 137.75, 137.50, 137.39, 135.53, 135.30, 134.19, 133.43, 132.97 (aryl *C*), 130.02 (aryl *C*), 128.61 (2C, aryl *C*), 128.35 (2C, aryl *C*), 127.71 (2C, aryl *C*), 127.09 (2C, aryl *C*), 126.17 (aryl *C*), 73.80 (sp^3-*C* of C_{60}), 73.10 (sp^3-*C* of C_{60}), 68.70, 54.82, 36.51, 19.41, 17.78 (2C); FT-IR ν/cm^{-1} (KBr) 3419, 3027, 2951, 2895, 1599, 1482, 1429, 1372, 1303, 1228, 1186, 1070, 1027, 906, 854, 762, 695, 667, 597, 571, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; HRMS (MALDI-TOF) *m/z*: [M]$^-$ Calcd for $C_{78}H_{21}N$ 971.1674; Found 971.1673.

Cyclopentafullerenes *trans*-3ad and ***cis*-3ad:** According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2d** (53.6 mg, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 60 min afforded first unreacted C_{60} (22.3 mg, 62%) and then *trans*-**3ad** (3.1 mg, 7%, R_f = 0.47), *cis*-**3ad** (13.1 mg, 28%, R_f = 0.29) as amorphous brown solid with

CS_2 as eluent: mp > 300 °C. *trans*-**3ad**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.58 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.12-6.10 (m, 1H), 5.67 (dd, J = 7.2, 5.3 Hz, 1H), 5.50 (dd, J = 14.3, 4.5 Hz, 1H), 3.76-3.70 (m, 1H), 2.96 (dd, J = 12.6, 4.6 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.02, 154.30, 152.67, 152.59, 145.63, 145.21 (2C), 145.10, 144.64, 144.29, 144.24, 144.22, 144.14, 144.08, 144.01 (2C), 143.97, 143.74, 143.62, 143.48, 143.42, 143.36 (2C), 143.29 (3C), 143.27, 143.25, 143.10, 142.69, 142.56 (2C), 142.48, 141.11, 141.05, 140.76, 140.59, 140.52 (2C), 140.43, 140.29, 140.25, 140.23, 140.18, 140.10, 139.98 (3C), 139.79, 139.72, 139.63, 138.36, 137.67, 137.51, 137.43, 136.76, 135.76, 134.42, 134.13, 133.21, 128.06 (2C, aryl *C*), 127.78 (2C, aryl *C*), 127.03 (2C, aryl *C*), 126.08 (aryl *C*), 123.98 (aryl *C*), 112.01 (2C, aryl *C*), 76.18 (sp^3-*C* of C_{60}), 73.40 (sp^3-*C* of C_{60}), 63.77, 55.35, 35.13, 19.24; FT-IR ν/cm^{-1} (KBr) 3396, 3019, 2948, 1617, 1516, 1456, 1383, 1303, 1249, 1185, 885, 807, 695, 670, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 309, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}N$ 943.1361; Found 943.1338. *cis*-**3ad**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.56 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 5.77-5.71 (m, 1H), 5.26 (d, J = 9.9 Hz, 1H), 4.93 (dd, J = 13.8, 4.4 Hz, 1H), 3.58-3.50 (m, 1H), 3.07-3.02 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.64, 152.93, 152.73, 152.36, 145.70, 145.43, 144.89, 144.86, 144.84, 143.98, 143.87 (2C), 143.78, 143.74, 143.72, 143.66 (3C), 143.46, 143.37, 143.27, 143.10, 142.99, 142.97, 142.90, 142.81, 142.78, 142.76 (2C), 142.36, 142.17, 142.09 (2C), 140.74, 140.64, 140.33, 140.29 (2C), 140.22 (2C), 140.03 (2C), 139.92, 139.81, 139.68, 139.64, 139.56, 139.42 (3C), 139.18, 137.53, 137.32, 137.31, 136.88, 135.50, 134.13, 134.03, 133.37, 132.37, 127.83 (2C, aryl *C*), 127.35 (2C, aryl *C*), 126.95 (2C, aryl *C*), 125.92 (aryl *C*), 123.52 (aryl *C*), 111.90 (2C, aryl *C*), 73.92 (sp^3-*C* of C_{60}), 73.66 (sp^3-*C* of C_{60}), 64.66, 54.18, 34.47, 18.97; FT-IR ν/cm^{-1} (KBr) 3413, 3024, 2908, 1614, 1515, 1455, 1426, 1356, 1295, 1249, 1223, 1185, 1141, 1011, 807, 761, 696, 666, 653, 571, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 430; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}N$ 943.1361; Found 943.1335.

Cyclopentafullerenes *trans*-3ae and *cis*-3ae: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2e** (63.8 mg, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 30 min afforded first unreacted C_{60} (25.1 mg, 70%) and then *trans*-**3ae** (5.1 mg, 11%, R_f = 0.64), *cis*-**3ae** (6.3 mg, 13%, R_f = 0.45) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *trans*-**3ae**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 9.1 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 5.71 (dd, *J* = 8.0, 5.4 Hz, 1H), 5.58 (dd, *J* = 14.4, 4.5 Hz, 1H), 3.80-3.73 (m, 1H), 2.90 (dd, *J* = 12.5, 4.3 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.40, 153.75, 152.04, 151.99, 145.07, 144.83 (2C), 144.65, 144.17 (2C), 143.90, 143.85, 143.83, 143.77, 143.70, 143.62 (2C), 143.59, 143.33, 143.19, 142.98 (2C), 142.90 (4C), 142.85, 142.71 (2C), 142.28, 142.16 (2C), 142.09, 140.72, 140.67, 140.37, 140.21, 140.13 (2C), 140.03, 139.82 (3C), 139.75, 139.70, 139.58 (3C), 139.40, 139.33, 139.23, 137.98, 137.29, 137.12, 137.07, 136.25, 135.43, 134.01, 133.70, 132.90, 127.40 (2C, aryl *C*), 126.92 (2C, aryl *C*), 126.79 (2C, aryl *C*), 125.87 (aryl *C*), 119.40 (aryl *C*), 112.62 (2C, aryl C), 75.71 (sp^3-*C* of C_{60}), 72.96 (sp^3-*C* of C_{60}), 63.11, 54.95, 34.66; FT-IR v/cm^{-1} (KBr) 3395, 3023, 2898, 2361, 1598, 1495, 1457, 1384, 1311, 1182, 1094, 903, 813, 761, 697, 615, 528; UV-vis ($CHCl_3$) λ_{max}/nm 256, 311, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{14}ClN$ 963.0815; Found 963.0753. *cis*-**3ae**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.57 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 9.5 Hz, 1H), 5.84-5.78 (m, 1H), 4.99 (dd, J = 13.9, 4.3 Hz, 1H), 3.62 (q, J = 12.6 Hz, 1H), 2.98-2.94 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.68, 153.15, 152.99, 152.56, 145.81, 145.54, 145.19, 145.16 (2C), 144.77, 144.30, 144.21, 144.19, 144.06 (3C), 143.99 (2C), 143.96, 143.75, 143.65, 143.42, 143.31, 143.29, 143.23, 143.11 (4C), 142.66, 142.46, 142.42 (2C), 141.07, 140.97, 140.65, 140.61 (2C), 140.55, 140.47, 140.34, 140.33, 140.22, 140.13, 140.00, 139.96, 139.87, 139.73 (2C), 139.70, 139.50, 137.86, 137.68 (2C), 137.21, 135.75, 134.44, 134.29, 133.67, 132.84, 127.61 (2C, aryl *C*), 127.27 (2C, aryl *C*), 127.18 (2C, aryl *C*), 126.15 (aryl *C*), 119.48 (aryl *C*), 113.11 (2C, aryl *C*), 74.08 (sp^3-*C* of C_{60}), 73.95 (sp^3-*C* of C_{60}), 64.53, 54.38, 34.52; FT-IR v/cm^{-1} (KBr) 3402, 3057, 3024, 2954, 1597, 1494, 1457, 1426, 1401, 1313, 1249, 1182, 1137, 1093, 1068, 1009, 813, 781, 762, 695, 668, 597, 571, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 430; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{14}ClN$ 963.0815; Found 963.0748.

Cyclopentafullerenes *trans*-3af and *cis*-3af: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **2f** (86.0 mg, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 50 min afforded first unreacted C_{60} (26.4 mg, 73%) and then *trans*-**3af** (4.4 mg, 9%, R_f = 0.80), *cis*-**3af** (6.2 mg, 12%, R_f = 0.63) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *trans*-**3af**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.59 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.70 (dd, J = 8.2, 5.4 Hz, 1H), 5.58 (dd, J = 14.4, 4.5 Hz, 1H), 3.80-3.73 (m, 1H), 2.89 (dd, J = 12.7, 4.5 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.40, 153.77, 152.06, 151.98, 145.09, 144.85 (2C), 144.67, 144.60, 144.19, 143.93, 143.88, 143.85, 143.79, 143.72, 143.64 (2C), 143.61, 143.35, 143.21, 143.01 (2C), 142.93 (5C), 142.88, 142.74, 142.31, 142.19 (2C), 142.11, 140.75, 140.69, 140.39, 140.24, 140.16 (2C), 140.06, 139.84 (3C), 139.77, 139.73, 139.61 (3C), 139.43, 139.35, 139.25, 138.01, 137.31, 137.15, 137.10, 136.27, 135.46, 134.03, 133.72, 132.94, 129.78 (2C, aryl *C*), 127.42 (2C, aryl *C*), 126.82 (2C, aryl *C*), 125.90 (aryl *C*), 113.15 (2C, aryl *C*), 106.84 (aryl *C*), 75.73 (sp^3-*C* of C_{60}), 72.98 (sp^3-*C* of C_{60}), 63.03, 54.97, 34.66; FT-IR ν/cm^{-1} (KBr) 3399, 3023, 2884, 2799, 1592, 1493, 1457, 1427, 1395, 1311, 1249, 1184, 1075, 929, 810, 763, 695, 570, 528; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{14}BrN$ 1007.0310; Found 1007.0259. *cis*-**3af**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.57 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 9.4 Hz, 1H), 5.83-5.78 (m, 1H), 4.99 (dd, *J* = 13.9, 4.2 Hz, 1H), 3.63 (q, *J* = 12.6 Hz, 1H), 3.10-2.93 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.59, 153.08, 152.91, 152.50, 145.72, 145.46, 145.11 (2C), 145.09 (2C), 144.22, 144.11 (2C), 143.98 (3C), 143.91 (3C), 143.68, 143.58, 143.34, 143.23, 143.21, 143.16, 143.03 (4C), 142.59, 142.39, 142.34 (2C), 140.99, 140.90, 140.58, 140.53 (2C), 140.47, 140.39, 140.27, 140.25, 140.14, 140.05, 139.93, 139.88, 139.79, 139.66 (2C), 139.62, 139.43, 137.78, 137.62 (2C), 137.13, 135.68, 134.36, 134.22, 133.60, 132.78, 130.05 (2C, aryl *C*), 127.55 (2C, aryl *C*), 127.14 (2C, aryl *C*), 126.12 (aryl *C*), 113.56 (2C, aryl *C*), 106.75 (aryl *C*), 73.99 (sp^3-*C* of C_{60}), 73.87 (sp^3-*C* of C_{60}), 64.33, 54.29, 34.42; FT-IR ν/cm^{-1} (KBr) 3403, 3064, 3026, 2950, 2883, 1591, 1492, 1457, 1426, 1398, 1311, 1248, 1182, 1139, 1071, 1008, 810, 781, 761, 695, 653, 570, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 430; HRMS (ESI) *m/z*: [M]$^-$ Calcd for $C_{75}H_{14}BrN$ 1007.0310; Found 1007.0251.

Cyclopentafullerenes *trans*-3ba and ***cis*-3ba:** According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (88.1 mg, 0.50 mmol), **2a** (46 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 40 min afforded first unreacted C_{60} (25.2 mg, 70%) and then *trans*-**3ba** (4.6 mg, 10%, R_f = 0.77), *cis*-**3ba** (7.8 mg, 16%, R_f = 0.67) as amorphous brown solid with CS_2/CH_2Cl_2 as eluent (V/V = 10/1): mp > 300 °C. *trans*-**3ba**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 7.2 Hz, 1H), 5.72-5.70 (m, 1H), 5.54 (dd, *J* = 14.3, 4.3 Hz, 1H), 3.74-3.68 (m, 1H), 3.71 (s, 3H), 2.88

(dd, J = 12.6, 4.3 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 156.77 (aryl *C*), 154.88, 154.28, 152.58, 152.40, 145.52, 145.42, 144.98 (2C), 144.89, 144.59, 144.06, 143.99 (2C), 143.92, 143.85, 143.77 (2C), 143.73, 143.52, 143.39, 143.23, 143.12, 143.03 (6C), 142.86, 142.46, 142.33 (2C), 142.28, 140.88, 140.81, 140.52, 140.36, 140.28 (2C), 140.20, 140.06, 140.03, 139.98 (2C), 139.87, 139.76 (2C), 139.72, 139.56, 139.53, 139.41, 138.11, 137.51, 137.36, 137.18, 135.59, 134.11, 133.85, 133.04, 128.49 (2C, aryl *C*), 128.30 (aryl *C*), 127.36 (2C, aryl *C*), 115.63 (aryl *C*), 112.24 (2C, aryl *C*), 111.60 (2C, aryl *C*), 75.89 (sp^3-*C* of C_{60}), 73.41 (sp^3-*C* of C_{60}), 63.21, 54.53, 53.83, 35.23; FT-IR ν/cm^{-1} (KBr) 3395, 2922, 2851, 1601, 1507, 1461, 1427, 1311, 1251, 1180, 1149, 1034, 829, 746, 690, 666, 570, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 308, 431; HRMS (ESI) *m/z*: [M]$^-$ Calcd for $C_{76}H_{17}NO$ 959.1310; Found 959.1257. *cis*-**3ba**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.47 (d, J = 8.6 Hz, 2H), 6.97 (t, J = 7.8 Hz, 2H), 6.83-6.79 (m, 4H), 6.47 (t, J = 7.3 Hz, 1H), 6.15 (d, J = 9.3 Hz, 1H), 5.83-5.78 (m, 1H), 4.93 (dd, J = 13.8, 4.4 Hz, 1H), 3.71 (s, 3H), 3.58 (q, J = 12.6 Hz, 1H), 2.96-2.92 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 156.63 (aryl *C*), 154.52, 153.10, 152.89, 152.42, 145.55 (2C), 145.32, 144.82, 144.76 (2C), 143.88 (2C), 143.80, 143.77, 143.65, 143.63, 143.56 (2C), 143.54, 143.38, 143.28, 143.00, 142.87 (2C), 142.81, 142.71 (2C), 142.67 (2C), 142.26, 142.07, 142.03, 142.01, 140.65, 140.55, 140.19 (3C), 140.13 (2C), 139.96 (2C), 139.83, 139.72, 139.56 (2C), 139.50, 139.36, 139.32 (2C), 139.11, 137.50, 137.20 (2C), 136.86, 134.05, 133.89, 133.20, 132.36, 128.17 (2C, aryl *C*), 127.27 (2C, aryl *C*), 127.14 (aryl *C*), 115.32 (aryl *C*), 112.26 (2C, aryl

C), 111.64 (2C, aryl *C*), 73.86 (sp^3-*C* of C_{60}), 73.77 (sp^3-*C* of C_{60}), 64.24, 53.76, 53.43, 34.62; FT-IR ν/cm^{-1} (KBr) 3391, 3022, 2946, 2889, 2826, 1601, 1508, 1457, 1430, 1308, 1251, 1180, 1033, 830, 747, 687, 651, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 308, 430; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}NO$ 959.1310; Found 959.1256.

Cyclopentafullerenes *trans*-3ca and *cis*-3ca: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (88.6 mg, 0.50 mmol), **2a** (46 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 40 min afforded first unreacted C_{60} (21.3 mg, 59%) and then *trans*-**3ca** (7.6 mg, 16%, R_f = 0.71), *cis*-**3ca** (10.9 mg, 22%, R_f = 0.65) as amorphous brown solid with CS_2/CH_2Cl_2 as eluent (V/V = 10/1): mp > 300 °C. *trans*-**3ca**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.16 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.6 Hz, 2H), 7.02 (t, J = 7.8 Hz, 2H), 6.93-6.89 (m, 3H), 6.53 (t, J = 7.2 Hz, 1H), 5.83-5.77 (m, 2H), 3.85-3.79 (m, 1H), 2.96 (dd, J = 12.6, 4.5 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.17, 153.01, 152.05, 150.98, 145.26, 145.08, 144.90 (2C), 144.84, 144.22 (2C), 143.97, 143.91, 143.85, 143.78, 143.73, 143.66 (2C), 143.63 (2C), 143.28, 143.20, 143.06, 142.98 (4C), 142.91 (3C), 142.78, 142.35, 142.23, 142.12, 142.02, 140.77, 140.71, 140.42, 140.25, 140.19, 140.15, 140.07, 139.90, 139.86 (2C), 139.68 (2C), 139.62, 139.54, 139.50, 139.41, 139.39, 139.29, 138.10, 137.38, 137.21, 137.11, 135.33, 134.43, 134.24, 132.77, 128.65 (2C, aryl *C*), 127.28 (2C, aryl *C*), 121.69 (2C, aryl *C*), 115.66 (aryl *C*), 111.50 (2C, aryl *C*), 75.88 (sp^3-*C* of C_{60}), 72.58 (sp^3-*C* of C_{60}), 63.17, 54.45, 34.77; FT-IR *ν*/cm^{-1} (KBr) 3394, 2954, 2883, 1600, 1519, 1501, 1427, 1344, 1315, 1252, 1184, 855, 748, 694, 670, 570, 527;

UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{14}N_2O_2$ 974.1055; Found 974.0982. *cis*-**3ca**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.49 (t, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 9.5 Hz, 1H), 5.92-5.86 (m, 1H), 5.19 (dd, *J* = 13.8, 4.4 Hz, 1H), 3.68 (q, *J* = 12.7 Hz, 1H), 3.03-2.99 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.18, 151.89, 151.79, 151.57, 145.41, 145.39, 145.06, 144.81, 144.73, 144.66, 144.22, 143.76 (2C), 143.72, 143.56 (2C), 143.50 (3C), 143.36, 143.21, 143.13, 142.96, 142.92 (2C), 142.84, 142.72 (3C), 142.58 (2C), 142.22, 142.03, 141.84 (2C), 140.59, 140.49, 140.14 (3C), 140.04, 139.99, 139.86, 139.75 (2C), 139.58, 139.49, 139.40 (2C), 139.21 (2C), 139.18, 139.04, 137.42, 137.24, 137.18, 136.77, 134.31, 133.82, 133.61, 132.21, 128.43 (2C, aryl *C*), 127.20 (2C, aryl *C*), 121.70 (2C, aryl *C*), 115.31 (aryl *C*), 111.55 (2C, aryl *C*), 73.68 (sp^3-*C* of C_{60}), 72.92 (sp^3-*C* of C_{60}), 64.05, 53.16, 34.00; FT-IR *ν*/cm^{-1} (KBr) 3394, 2921, 2851, 1597, 1515, 1462, 1428, 1343, 1314, 1252, 1181, 1147, 1104, 1011, 852, 779, 747, 693, 593, 570, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 307, 430; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{75}H_{14}N_2O_2$ 974.1055; Found 974.0985.

Cyclopentafullerenes *trans*/*cis*-3da: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (71 μL, 0.50 mmol), **2a** (46 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 40 min afforded first unreacted C_{60} (30.2 mg, 84%) and then *trans*/*cis*-**3ca** (6.1 mg, 13%, *trans*/*cis* = 1/4, R_f = 0.73) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**3da**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.92 (br.s, 2H), 7.47 (t, *J* =

7.3 Hz, 2H), 7.34 (t, J = 7.1 Hz, 1H), 6.95 (t, J = 7.6 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.45 (t, J = 7.1 Hz, 1H), 6.20 (d, J = 9.5 Hz, 1H), 5.77-5.70 (m, 1H), 5.01 (d, J = 7.5 Hz, 1H), 3.84-3.76 (m, 1H), 1.16 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 157.64, 154.80, 153.21, 152.60, 146.26, 146.08, 145.62, 145.14, 145.06, 144.76, 144.17, 144.01, 143.92 (3C), 143.87 (2C), 143.72, 143.57, 143.30 (2C), 143.12 (2C), 143.06, 143.00 (2C), 142.95, 142.91, 142.79, 142.56, 142.39 (2C), 142.25, 140.94, 140.90, 140.53, 140.49, 140.37, 140.34, 140.14, 140.03 (2C), 140.01, 139.97, 139.81 (3C), 139.71 (2C), 139.53, 139.46, 137.93, 137.91, 137.69, 137.55 (2C), 135.62, 133.57, 133.38, 132.25, 128.88 (2C, aryl *C*), 127.43 (2C, aryl *C*), 127.17 (2C, aryl *C*), 125.98 (aryl *C*), 115.41 (aryl *C*), 111.57 (2C, aryl *C*), 73.83 (sp^3-*C* of C_{60}), 71.26 (sp^3-*C* of C_{60}), 68.28, 59.49, 40.96, 12.14; FT-IR ν/cm^{-1} (KBr) 3407, 3012, 2883, 1599, 1501, 1455, 1429, 1384, 1311, 1252, 1185, 1144, 939, 748, 670, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 310, 431; HRMS (ESI) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}N$ 943.1361; Found 943.1302.

General Procedure for the Synthesis of Cyclopentafullerenes 5. A mixture of C_{60} (36.0 mg, 0.05 mmol), cinnamaldehydes **1** (0.50 mmol), secondary amines **4** (1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (8.9 mg, 0.025 mmol) was added to a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. After they were completely dissolved in 10 mL of chlorobenzene by sonication, the resulting solution was put into an oil bath preset at 80 ^{o}C and stirred under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60} and then cyclopentafullerenes **5**.

Cyclopentafullerene *cis*-5aa and Fulleropyrrolidine *trans*-6aa: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4a** (103 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 60 min afforded first unreacted C_{60} (17.9 mg, 50%) and then *cis*-**5aa**[1] (18.3 mg, 40%, R_f = 0.82) and *trans*-**6aa**[2,3] (3.8 mg, 8%, R_f = 0.24) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

Cyclopentafullerene *cis*-5ab and Fulleropyrrolidine *trans*-6ab: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4b** (137 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 55 min afforded first unreacted C_{60} (22.7 mg, 63%) and then *cis*-**5ab** (13.9 mg, 30%, R_f = 0.97) and *trans*-**6ab**[3] (trace, R_f = 0.68) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.58 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 5.04 (dd, J = 12.5, 4.5 Hz, 1H), 4.86 (dd, J = 13.4, 4.5 Hz, 1H), 3.60 (q, J = 12.6 Hz, 1H), 3.06 (br.s, 2H), 2.99-2.93 (m, 2H), 2.89-2.84 (m, 1H), 1.71-1.61 (m, 2H), 1.56-1.50 (m, 2H), 0.91-0.86 (m, 6H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.39, 154.80, 153.00, 152.70, 146.17, 145.78, 145.40, 145.23, 144.81, 144.49, 144.43, 144.41, 144.34 (2C), 144.24, 144.19, 144.09, 144.03, 144.01, 143.85, 143.52, 143.45, 143.39 (2C), 143.35, 143.30 (2C), 143.17, 142.84, 142.70, 142.61, 142.52, 141.36, 141.20, 140.84, 140.79 (2C), 140.68, 140.61, 140.48 (2C), 140.39, 140.33, 140.20, 140.16, 139.99, 139.95 (2C), 139.85, 139.78, 138.15, 137.70, 137.64, 137.44, 136.09 (aryl *C*), 134.40, 134.00, 133.16, 132.61, 127.77 (2C, aryl *C*), 127.22 (2C, aryl *C*), 126.22 (aryl *C*), 75.07, 74.31, 73.36, 55.42, 29.59, 21.01 (2C), 10.72 (2C); FT-IR ν/cm^{-1} (KBr) 2958, 2926, 2865, 2793, 1516, 1459, 1427, 1376, 1189, 1088, 1013, 759, 696, 573, 547, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 311, 431; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{75}H_{23}N$ 937.1831; Found 937.1832.

Cyclopentafullerene *cis*-5ac and Fulleropyrrolidine *trans*-6ac: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4c** (169 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3\cdot xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 50 min afforded first unreacted C_{60} (17.4 mg, 48%) and then *cis*-**5ac** (21.5 mg, 45%, R_f = 0.97) and *trans*-**6ac**[3] (trace, R_f = 0.84) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**5ac**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.57 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 5.03-4.99 (m, 1H), 4.84-4.81 (m, 1H), 3.57 (q, J = 12.6 Hz, 1H), 3.09 (br.s, 2H), 2.94 (br.s, 2H), 2.87-2.83 (m, 1H), 1.63-1.61 (m, 2H), 1.45 (br.s, 2H), 1.33-1.26 (m, 4H), 0.87 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.40, 154.90, 153.13, 152.77, 146.22, 145.88, 145.45, 145.28, 144.88, 144.54, 144.49, 144.46, 144.39 (2C), 144.28, 144.23, 144.15, 144.08 (2C), 143.91, 143.57, 143.51, 143.46, 143.44, 143.39, 143.35 (2C), 143.21, 142.89, 142.76, 142.67, 142.57, 141.41, 141.25, 140.88, 140.85 (2C), 140.73, 140.62, 140.55, 140.53, 140.43, 140.39, 140.25, 140.21, 139.99 (3C), 139.94, 139.84, 138.15, 137.73, 137.70, 137.48, 136.17, 134.41, 134.07, 133.25, 132.64, 127.83 (2C, aryl *C*), 127.28 (2C, aryl *C*), 126.26 (aryl *C*), 75.13, 74.32, 73.34, 55.49, 29.78 (2C), 29.42, 19.43 (2C), 13.06 (2C); FT-IR ν/cm^{-1} (KBr) 2954, 2925, 2858, 1539, 1498, 1458, 1427, 1372, 1269, 1221, 1185, 1013, 896, 828, 760, 695, 573, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 311, 431; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{77}H_{27}N$ 965.2144; Found 965.2142.

Cyclopentafullerene *cis*-5ad and Fulleropyrrolidine *trans*-6ad: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4d** (129 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 15 min afforded first unreacted C_{60} (14.3 mg, 40%) and then *cis*-**5ad** (20.1 mg, 42%, R_f = 0.88) and *trans*-**6ad**[3] (4.4 mg, 9%, R_f = 0.10) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**5ad**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.32-7.28 (m, 4H), 7.22-7.13 (m, 4H), 5.08 (d, *J* = 11.2 Hz, 1H), 4.85 (d, *J* = 12.6 Hz, 1H), 4.31 (d, *J* = 13.3 Hz, 1H), 4.13 (d, *J* = 13.3 Hz, 1H), 3.62 (q, *J* = 12.5 Hz, 1H), 2.95-2.93 (m, 1H), 2.78 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.33, 154.68, 152.93, 152.71, 145.94, 145.88, 145.51, 145.38, 144.96, 144.55 (3C), 144.47 (2C), 144.35, 144.30, 144.23, 144.19, 144.13, 143.97, 143.64, 143.60, 143.55, 143.51, 143.48, 143.43 (2C), 143.33, 142.92, 142.83, 142.77, 142.63, 141.45, 141.33, 140.98, 140.92 (2C), 140.82, 140.73, 140.62, 140.57, 140.52, 140.45, 140.33, 140.28, 140.15, 140.13, 140.07, 140.06, 139.93, 138.19, 137.98, 137.86, 137.61, 137.44, 136.17, 134.58, 134.41, 133.36, 132.88, 127.93 (2C, aryl *C*), 127.36 (4C, aryl *C*), 126.98 (2C, aryl *C*), 126.35 (aryl *C*), 125.94 (aryl *C*), 75.83, 74.24, 73.57, 55.39, 29.06; FT-IR ν/cm^{-1} (KBr) 3027, 2922, 2848, 2787, 1602, 1538, 1494, 1454, 1427, 1359, 1217, 1184, 1071, 1027, 967, 907, 739, 696, 573, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{77}H_{19}N$ 957.1518; Found 957.1515.

Cyclopentafullerene *cis*-5ae and Fulleropyrrolidine *trans*-6ae: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4e** (192 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 150 min afforded first unreacted C_{60} (18.1 mg, 50%) and then *trans*-**6ae**[3] (5.9 mg, 11%, R_f = 0.89) and *cis*-**5ae** (15.4 mg, 30%, R_f = 0.75) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**5ae**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 4H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.22-7.12 (m, 7H), 5.08 (dd, *J* = 12.6, 4.5 Hz, 1H), 4.76 (dd, *J* = 13.5, 4.4 Hz, 1H), 3.96-3.92 (m, 2H), 3.66 (q, *J* = 12.6 Hz, 1H), 3.03-2.99 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.40, 154.12, 151.95, 151.42, 145.26, 145.22, 144.84, 144.72, 144.14, 143.96, 143.88, 143.82 (2C), 143.76, 143.67, 143.61, 143.59, 143.52, 143.45, 143.25, 142.99, 142.95, 142.85, 142.81, 142.74 (3C), 142.66, 142.18 (2C), 142.07, 141.94, 140.72, 140.65, 140.33, 140.25 (2C), 140.14, 140.06, 139.99, 139.88 (2C), 139.76, 139.67 (2C), 139.52, 139.35 (4C), 137.33, 137.11 (2C), 136.98, 136.79, 136.74, 135.54, 134.11, 133.89, 132.54, 131.91, 127.38 (2C, aryl *C*), 127.05 (aryl *C*), 126.89 (4C, aryl *C*), 126.50 (5C, aryl *C*), 125.92 (aryl *C*), 125.58 (2C, aryl *C*), 73.01, 72.96, 71.50, 54.76, 27.82; FT-IR ν/cm^{-1} (KBr) 3025, 2921, 2847, 2798, 1493, 1454, 1428, 1365, 1184, 1151, 1070, 1025, 970, 905, 782, 739, 696, 572, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 432; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{83}H_{23}N$ 1033.1831; Found 1033.1831.

Cyclopentafullerene *cis*-5af: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4f** (108 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (8.9 mg, 0.025 mmol) in ODCB (6 mL) at 180 °C for 120 min afforded first unreacted C_{60} (20.6 mg, 57%) and then *cis*-**5af** (8.5 mg, 18%, R_f = 0.87) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**5af**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.19 (dd, *J* = 12.3, 4.5 Hz, 1H), 5.07 (dd, *J* = 13.4, 4.4 Hz, 1H), 3.97 (q, *J* = 12.5 Hz, 1H), 3.35 (s, 3H), 2.93-2.89 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.20, 154.00, 152.80, 152.35, 148.49 (aryl *C*), 145.35, 145.29, 145.20 (2C), 145.02, 144.40, 144.35, 144.32 (2C), 144.28, 144.19, 144.14, 144.10 (2C), 143.89, 143.81, 143.52, 143.48 (2C), 143.38, 143.33, 143.25 (3C), 142.73, 142.62, 142.55, 142.51, 141.28, 141.18, 140.79, 140.76 (2C), 140.69, 140.54, 140.47, 140.39, 140.30 (2C), 140.14, 140.11, 140.02, 139.97, 139.91, 139.77 (2C), 138.16 (2C), 137.81, 137.43, 135.81, 134.43, 134.34, 133.59, 132.83, 127.81 (2C, aryl *C*), 127.73 (2C, aryl *C*), 127.25 (2C, aryl *C*), 126.31 (aryl *C*), 116.81 (aryl *C*), 112.61 (2C, aryl *C*), 73.86, 73.77, 71.60, 54.28, 33.06, 31.81; FT-IR *ν*/cm^{-1} (KBr) 3026, 2807, 1594, 1503, 1426, 1400, 1314, 1242, 1184, 1156, 1121, 1089, 1009, 963, 748, 693, 572, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 307, 430; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}N$ 943.1361; Found 943.1362.

Cyclopentafullerene *cis*-5ag: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), **4g** (126 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (8.9 mg, 0.025 mmol) in ODCB (6 mL) at 180 °C for 100 min afforded first unreacted C_{60} (27.2 mg, 76%) and then *cis*-**5ag** (6.8 mg, 14%, R_f = 0.91) as amorphous brown solid with CS_2 as eluent: mp > 300 °C. *cis*-**5ag**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) *δ* 7.64 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.63 (t, *J* = 6.9 Hz, 1H), 6.19 (dd, *J* = 12.1, 3.9 Hz, 1H), 5.05 (dd, *J* = 13.3, 3.9 Hz, 1H), 4.14-4.07 (m, 1H), 3.94 (q, *J* = 12.3 Hz, 1H), 3.76-3.69 (m, 1H), 2.99-2.96 (m, 1H), 1.31 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) *δ* 154.18, 153.71, 152.73, 152.14, 146.12 (aryl *C*), 145.05 (3C), 144.91, 144.77, 144.11, 144.05, 144.02 (2C), 143.97, 143.89, 143.84, 143.81 (2C), 143.61, 143.52, 143.18 (3C), 143.09, 143.04, 142.98, 142.93, 142.90, 142.45, 142.32, 142.24 (2C), 140.99, 140.89, 140.48 (3C), 140.40, 140.27, 140.17, 140.11, 140.02 (2C), 139.85 (2C), 139.71, 139.69, 139.61, 139.47, 139.40, 137.80 (2C), 137.54, 137.13, 135.55, 134.09, 134.05, 133.32, 132.31, 127.58 (4C, aryl *C*), 127.03 (2C, aryl *C*), 126.12 (aryl *C*), 116.54 (aryl *C*), 113.40 (2C, aryl *C*), 73.56 (2C), 70.78, 54.06, 32.21, 12.38; FT-IR ν/cm^{-1} (KBr) 3028, 2968, 2923, 2848, 1595, 1539, 1497, 1456, 1427, 1373, 1305, 1268, 1231, 1189, 1157, 1122, 1094, 1009, 745, 696, 573, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{77}H_{19}N$ 957.1518; Found 957.1516.

Cyclopentafullerene *cis*-5ba and Fulleropyrrolidine *trans*-6ba: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (81.1 mg, 0.50 mmol), **4a** (103 μL, 1.00 mmol), $Mg(ClO_4)_2$ (5.6 mg, 0.025 mmol) and $Fe(ClO_4)_3\cdot xH_2O$ (8.9 mg, 0.025 mmol) in chlorobenzene (10 mL) at 80 °C for 120 min afforded first unreacted C_{60} (21.3 mg, 59%) and then *cis*-**5ba**[1,4] (16.2 mg, 34%, R_f = 0.31) and *trans*-**6ba**[2,3] (trace, R_f = 0.06) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

Cyclopentafullerene *cis*-5ca and Fulleropyrrolidine *trans*-6ca: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (88.6 mg, 0.50 mmol), **4a** (103 μL, 1.00 mmol), $Mg(ClO_4)_2$ (11.2 mg, 0.05 mmol) and $Fe(ClO_4)_3\cdot xH_2O$ (17.8 mg, 0.05 mmol) in chlorobenzene (10 mL) at 80 °C for 35 min afforded first unreacted C_{60} (6.8 mg, 19%) and then *cis*-**5ca**[1] (6.4 mg, 13%, R_f = 0.15) and *trans*-**6ca**[2,3] (20.0 mg, 42%, R_f = 0.12) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

Reaction of C_{60} with Cinnamaldehyde (1a) and Triethylamine in the Presence of $Mg(ClO_4)_2$. By following the same experimental procedure as for the reaction of C_{60} with amines **2**/**4**, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (63 μL, 0.50 mmol), triethylamine (69 μL, 0.50 mmol) and $Mg(ClO_4)_2$ (44.7 mg, 0.20 mmol) in *o*-

dichlorobenzene (6 mL) at 180 °C for 60 min afforded first unreacted C_{60} (20.6 mg, 57%) and then *cis*-**5aa**[1] (9.9 mg, 22%, R_f = 0.82) and *trans*-**6aa**[2,3] (1.5 mg, 3%, R_f = 0.24) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

Cyclopentafullerene *cis*-7: By following the same experimental procedure as for the reaction of C_{60} with amines **2**/**4**, the reaction of *cis*-**3aa** (11.6 mg, 0.0125 mmol) with benzoyl chloride (29 μL, 0.250 mmol) and DMAP (7.6 mg, 0.0625 mmol) in chlorobenzene (5 mL) at 120 °C for 24 h afforded first unreacted *cis*-**3aa** (2.3 mg, 20%, R_f = 0.98) and then *cis*-**7** (10.2 mg, 79%, R_f = 0.36) as an amorphous brown solid (mp > 300 °C) with CS_2/CH_2Cl_2 as eluent (V/V = 10/1). *cis*-**7**: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.48 (d, J = 7.4 Hz, 2H), 7.28-7.17 (m, 7H), 7.10-7.00 (m, 6H), 5.12 (dd, J = 13.6, 4.2 Hz, 1H), 3.47-3.40 (m, 1H), 2.90-2.86 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 169.84 (*C*=O), 156.28, 153.70, 152.86, 152.21, 145.64 (2C), 145.59, 145.22, 145.04, 144.70, 144.61, 144.56 (3C), 144.46, 144.39 (3C), 144.25, 144.02, 143.87, 143.72, 143.66, 143.57, 143.50, 143.49, 143.42, 143.04, 142.91, 142.79 (2C), 141.48 (2C), 141.23, 141.03 (3C), 140.96, 140.91, 140.79, 140.69, 140.57, 140.34, 140.24, 140.16, 140.11, 140.03, 139.95, 139.60 (aryl *C*), 138.21, 138.10, 137.83, 137.82, 135.88 (aryl *C*), 135.02, 134.89, 134.54, 134.32, 132.43 (aryl *C*), 129.80 (2C, aryl *C*), 128.07 (aryl *C*), 128.01 (2C, aryl *C*), 127.78 (2C, aryl *C*), 127.39 (2C, aryl *C*), 127.03 (2C, aryl *C*), 126.61 (aryl *C*), 126.51 (aryl *C*), 126.39 (2C, aryl *C*), 74.43, 73.36, 66.37, 54.32, 33.29; FT-IR ν/cm^{-1} (KBr) 2920, 2849, 1644, 1593, 1491, 1453, 1426, 1337, 1267, 1218, 1180, 1155, 1108, 1073, 1016, 783, 762, 734, 697, 574, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 433; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{82}H_{19}NO$ 1033.1467; Found 1033.1468.

Cyclopentafullerene 8: By following the same experimental procedure as for the reaction of C_{60} with amines **2**/**4**, the reaction of *cis*-**3aa** (11.6 mg, 0.0125 mmol) with paraformaldehyde (0.8 mg, 0.0250 mmol) and TsOH·H_2O (2.4 mg, 0.0125 mmol) in chlorobenzene (5 mL) at 40 ^oC for 1.5 h afforded first unreacted *cis*-**3aa** (2.5 mg, 22%, R_f = 0.98) and then **8** (7.5 mg, 63%, *cis-ortho*-**8**/*trans-ortho*-**8** = 10.5/1, R_f = 0.86) as an amorphous brown solid (mp > 300 °C) with CS_2/CH_2Cl_2 as eluent (V/V = 10/1). *cis-ortho*-**8**: ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.63 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.24-7.16 (m, 2H), 7.11 (t, J = 8.0 Hz, 1H), 6.91-6.82 (m, 2H), 5.84 (dd, J = 12.4, 4.6 Hz, 1H), 5.56 (d, J = 10.6 Hz, 1H), 4.95-4.87 (m, 1H), 4.67 (d, J = 10.6 Hz, 1H), 3.91 (q, J = 12.8 Hz, 1H), 3.03-2.98 (m, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.55, 154.38, 152.87, 152.08, 146.08, 145.79. 145.71, 145.63, 145.26, 144.88, 144.75 (3C), 144.70, 144.63 (2C), 144.49, 144.47, 144.33, 144.17 (2C), 144.01, 143.88 (2C), 143.85 (2C), 143.72, 143.67 (2C), 143.12, 143.03 (2C), 142.99, 141.68, 141.60, 141.22 (2C), 141.14, 141.10, 140.90 (2C), 140.77, 140.75, 140.66, 140.60, 140.55, 140.40 (2C), 140.37, 140.23, 140.18, 138.74, 138.35, 138.21, 137.89, 136.03, 135.24, 134.83, 133.84, 133.69, 128.17 (2C, aryl *C*), 127.52 (2C, aryl *C*), 126.55 (aryl *C*), 126.38 (aryl *C*), 124.04 (aryl *C*), 123.73 (aryl *C*), 120.03 (aryl *C*), 118.07 (aryl *C*), 74.90, 74.18, 73.69, 66.54, 55.12, 32.35; FT-IR ν/cm^{-1} (KBr) 2919, 2849, 1603, 1491, 1455, 1427, 1270, 1225, 1179, 1056, 1030, 921, 750, 697, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 307, 431; HRMS (MALDI-TOF) *m/z*: $[M]^-$ Calcd for $C_{76}H_{17}NO$ 959.1310; Found 959.1311.

Transformation of *cis*-3aa in the Presence of $Mg(ClO_4)_2$. By following the same experimental procedure as for the reaction of C_{60} with amines **2**/**4**, the reaction of *cis*-**3aa** (18.6 mg, 0.02 mmol) with $Mg(ClO_4)_2$ (9.0 mg, 0.04 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first *trans*-**3aa** (4.3 mg, 24%, R_f = 0.68) and then unreacted *cis*-**3aa** (11.5 mg, 62%, R_f = 0.59) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

Transformation of *trans*-3aa in the Presence of $Mg(ClO_4)_2$. By following the same experimental procedure as for the reaction of C_{60} with amines **2**/**4**, the reaction of *trans*-**3aa** (18.6 mg, 0.02 mmol) with $Mg(ClO_4)_2$ (9.0 mg, 0.04 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 60 min afforded first C_{60} (1.3 mg, 9%) and then unreacted *trans*-**3aa** (1.7 mg, 8%, R_f = 0.68), *cis*-**3aa** (7.4 mg, 40%, R_f = 0.59) as amorphous brown solid with CS_2 as eluent: mp > 300 °C.

References

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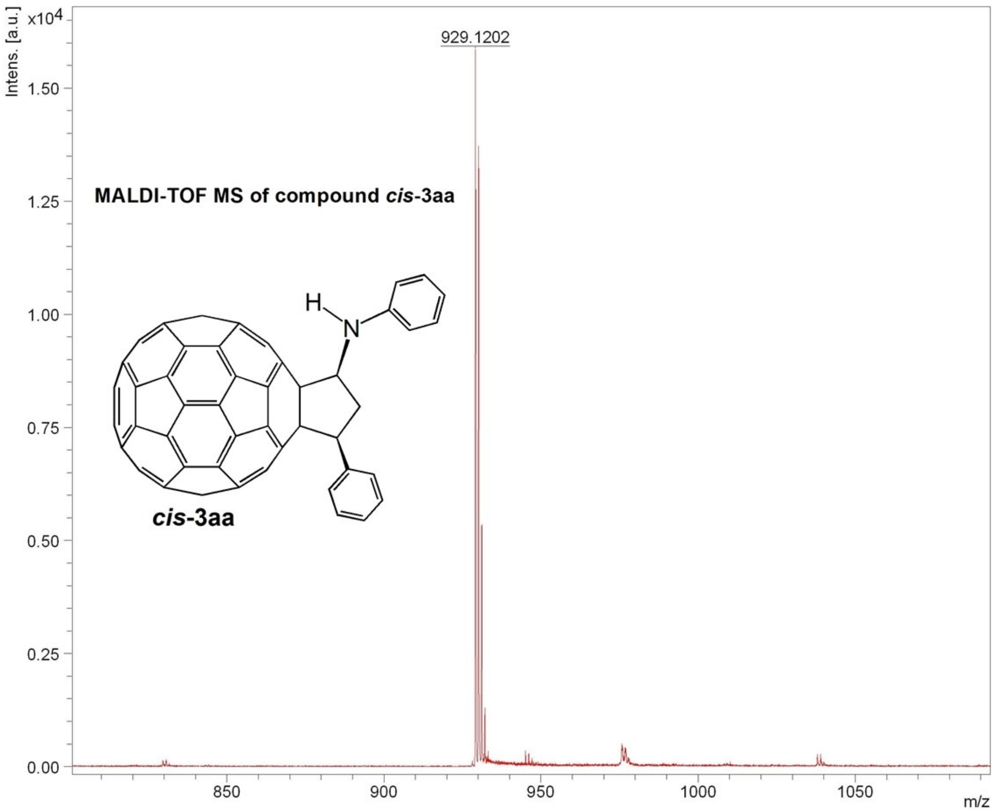
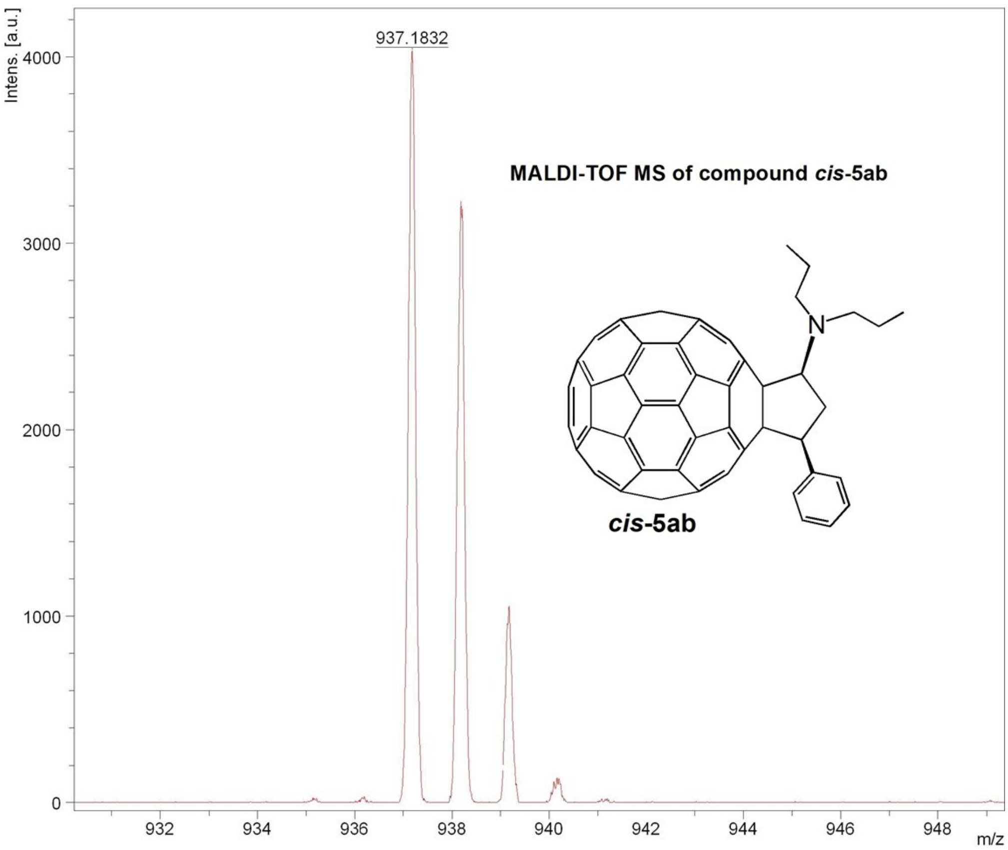
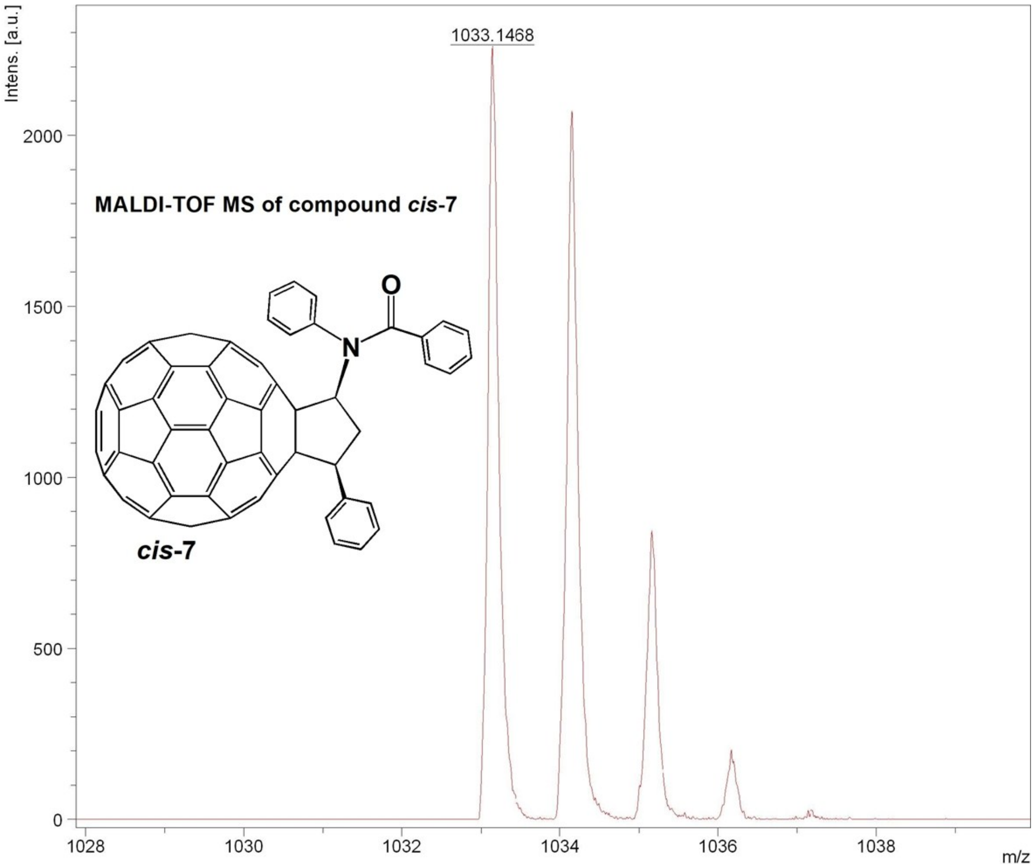
4 G.-W. Wang, X.-P. Chen and X. Cheng, *Chem. Eur. J,* 2006, **12**, 7246.

Typical MALDI-TOF MS of cyclopentafullerenes







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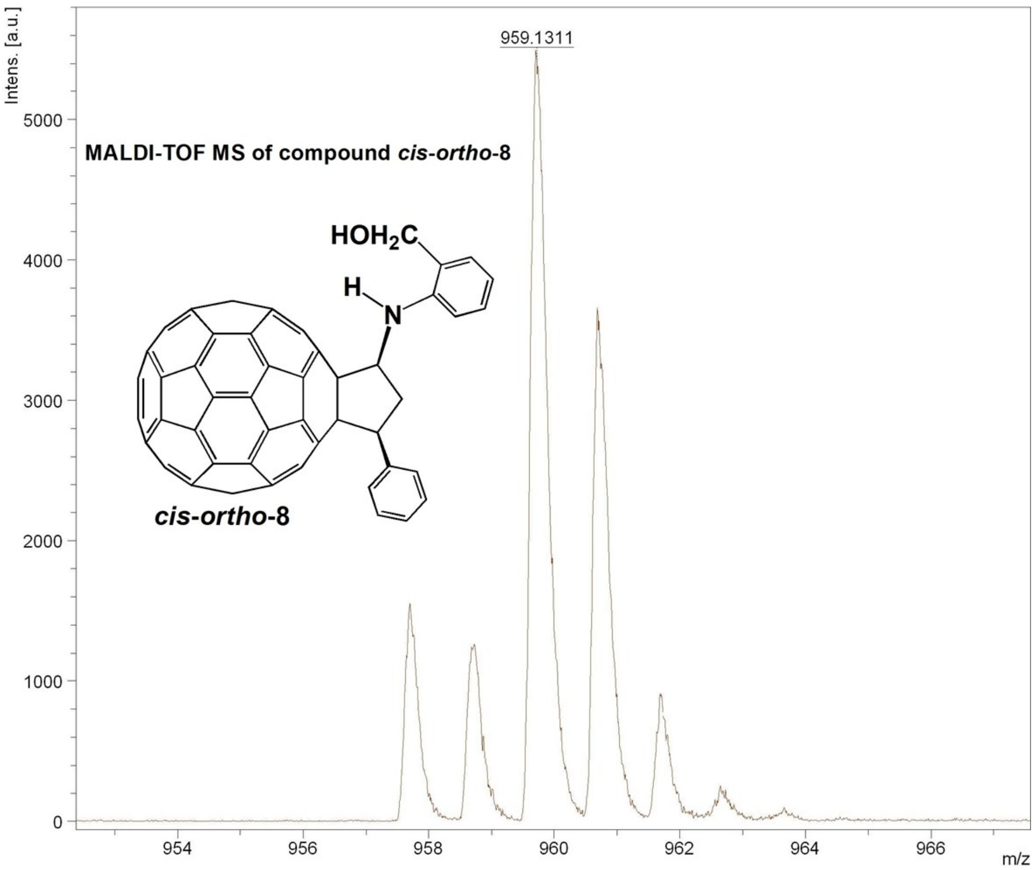
m/z



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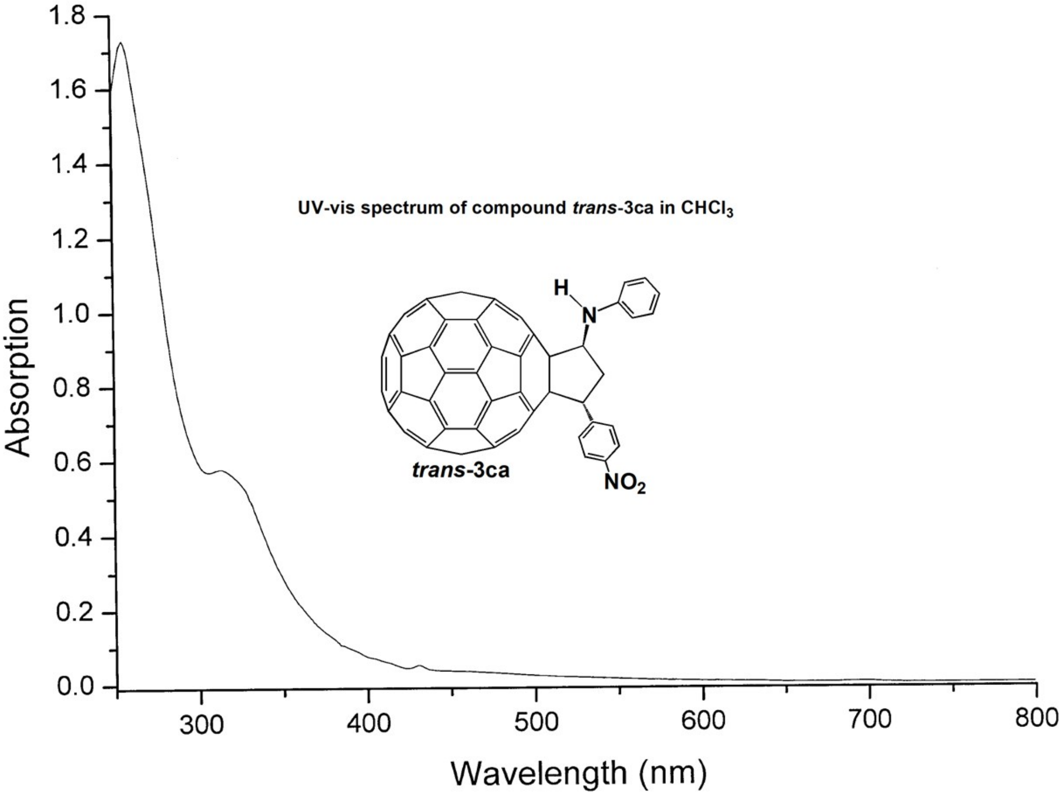
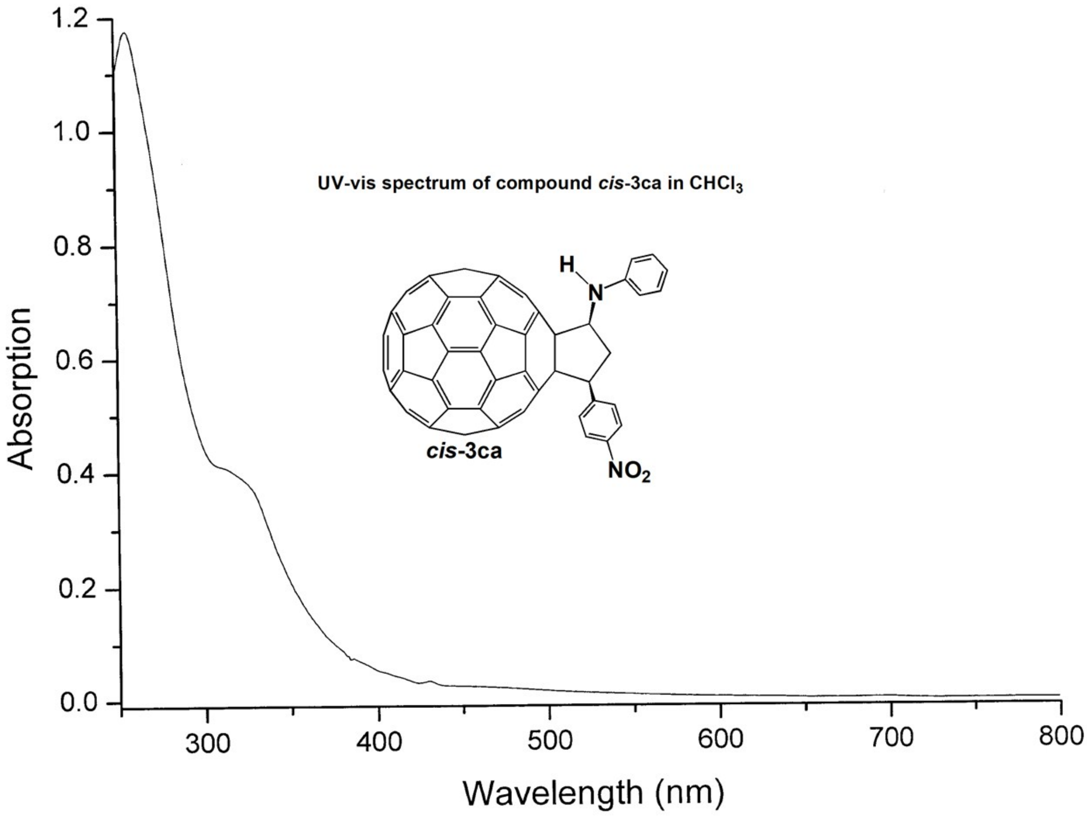
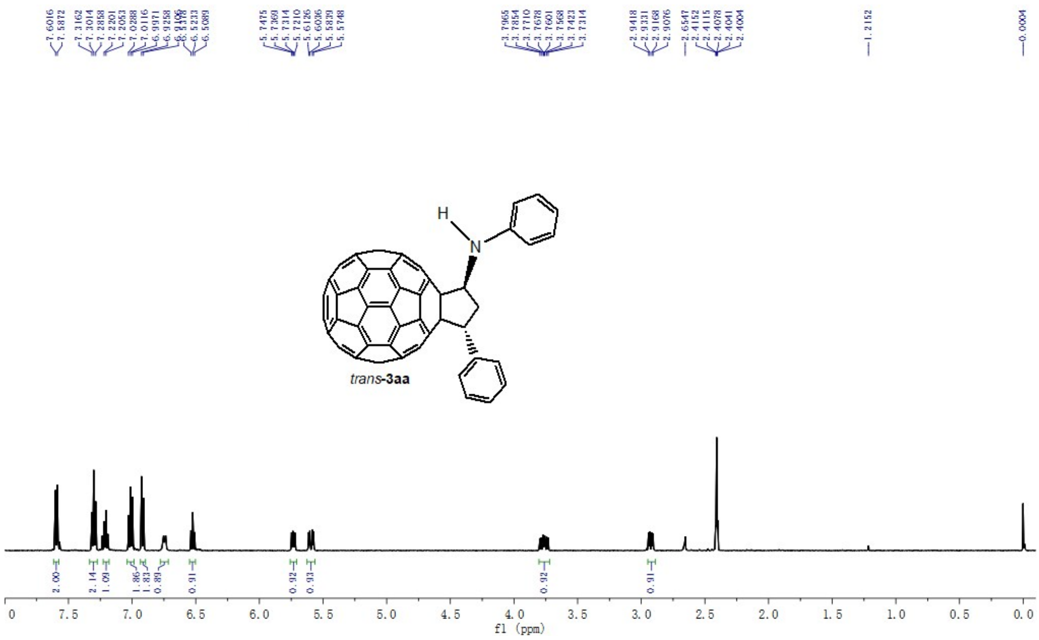
m/z

Typical UV-vis spectra of cyclopentafullerenes

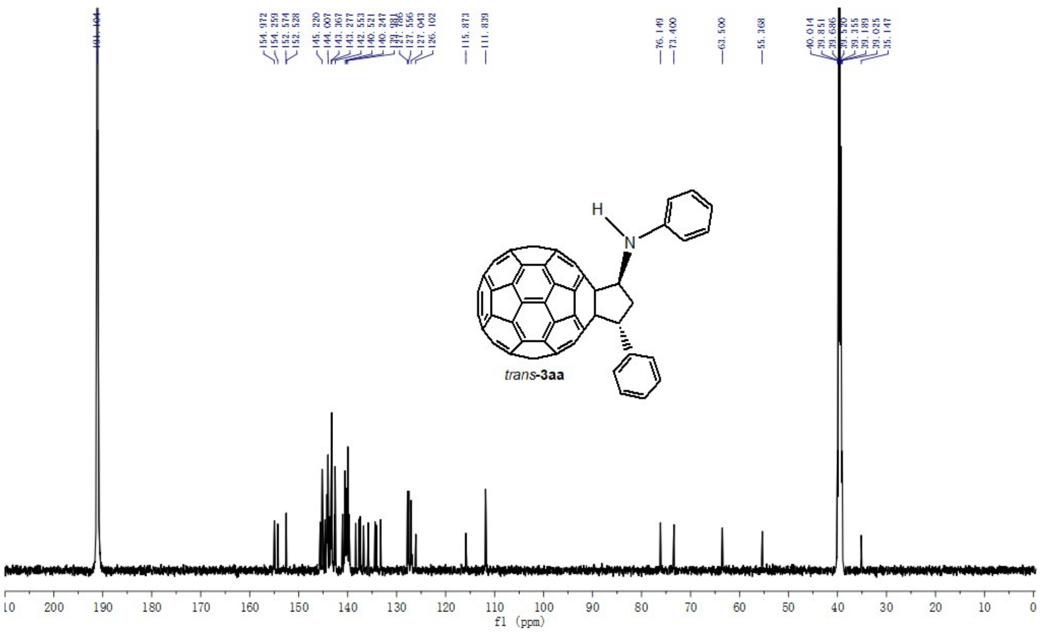


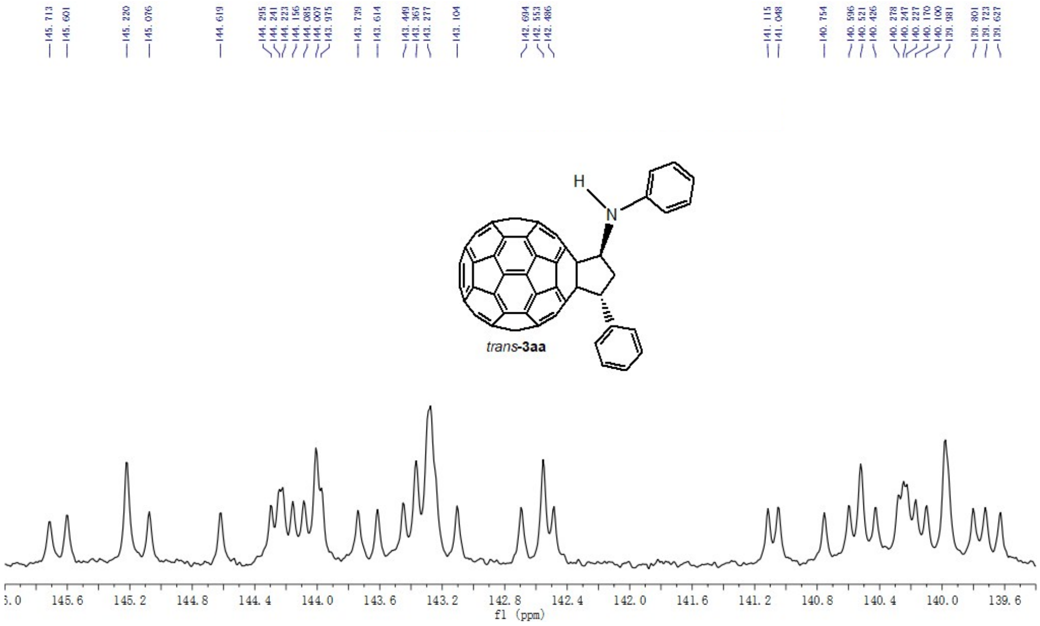


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3aa**



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3aa**





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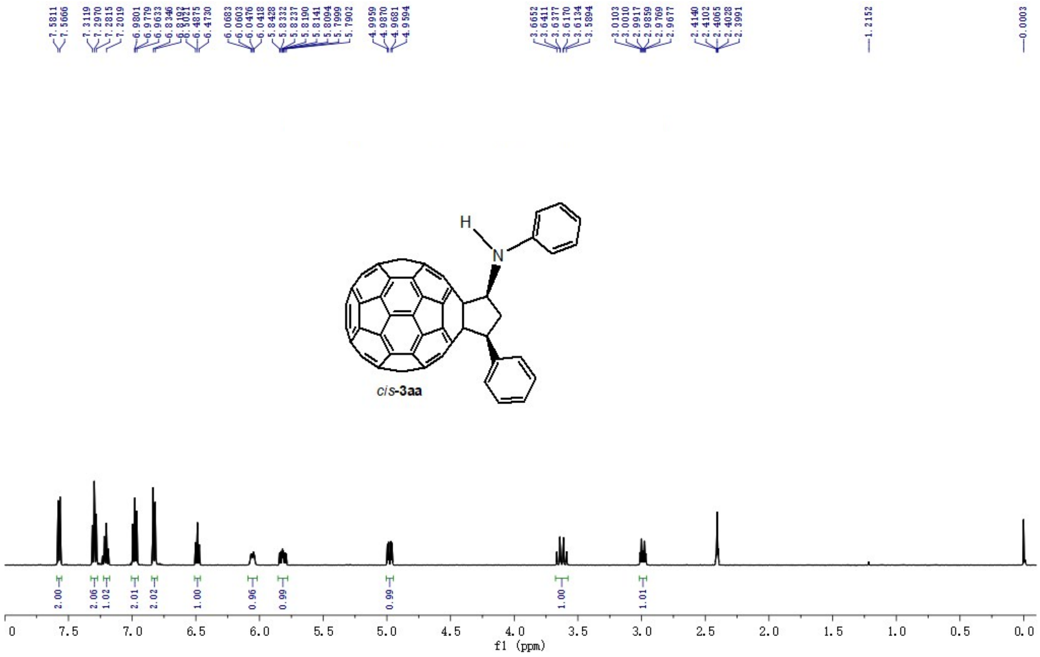

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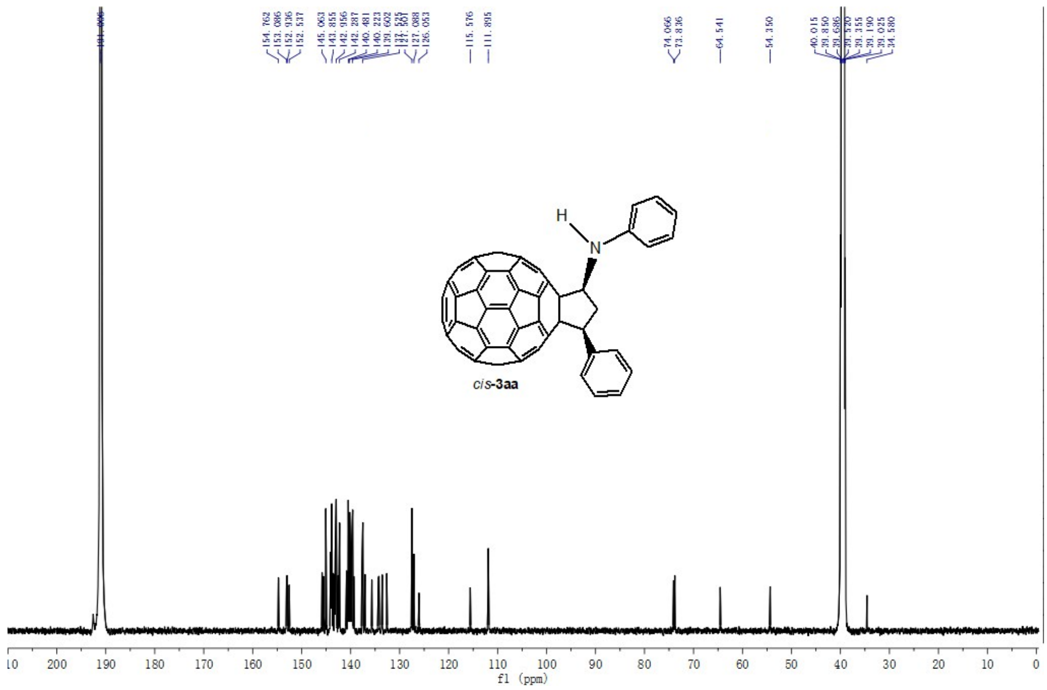
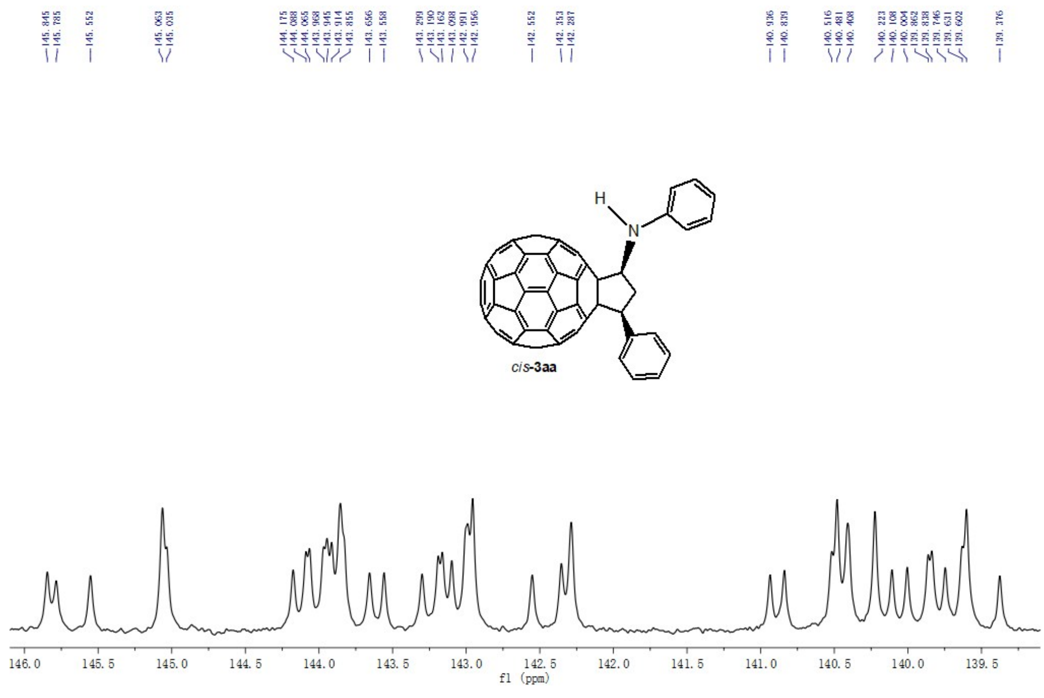
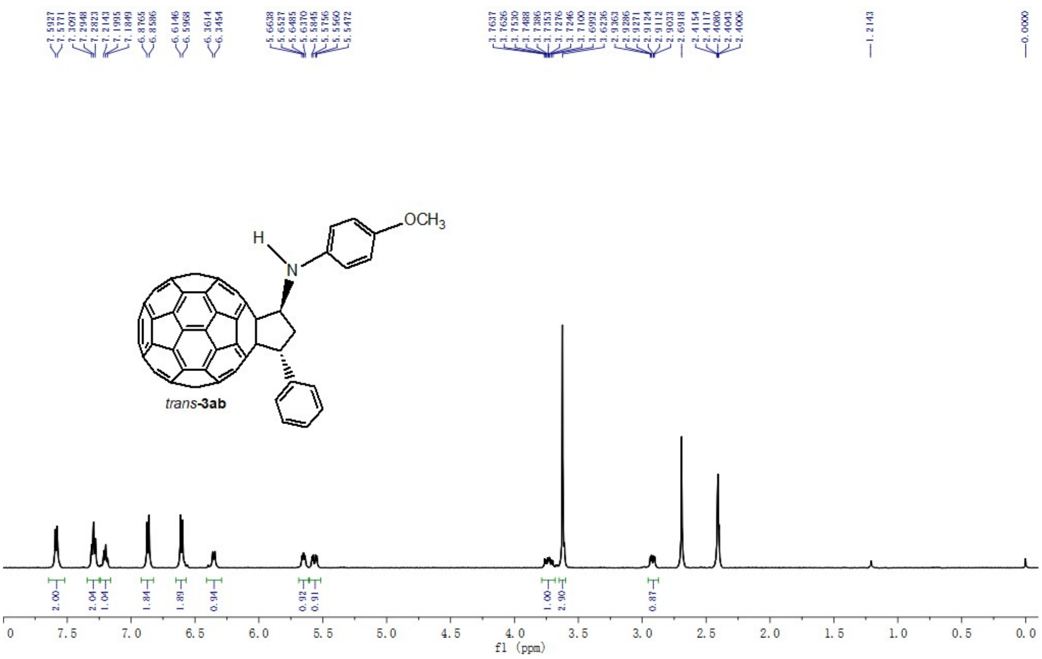




[1]H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ab**



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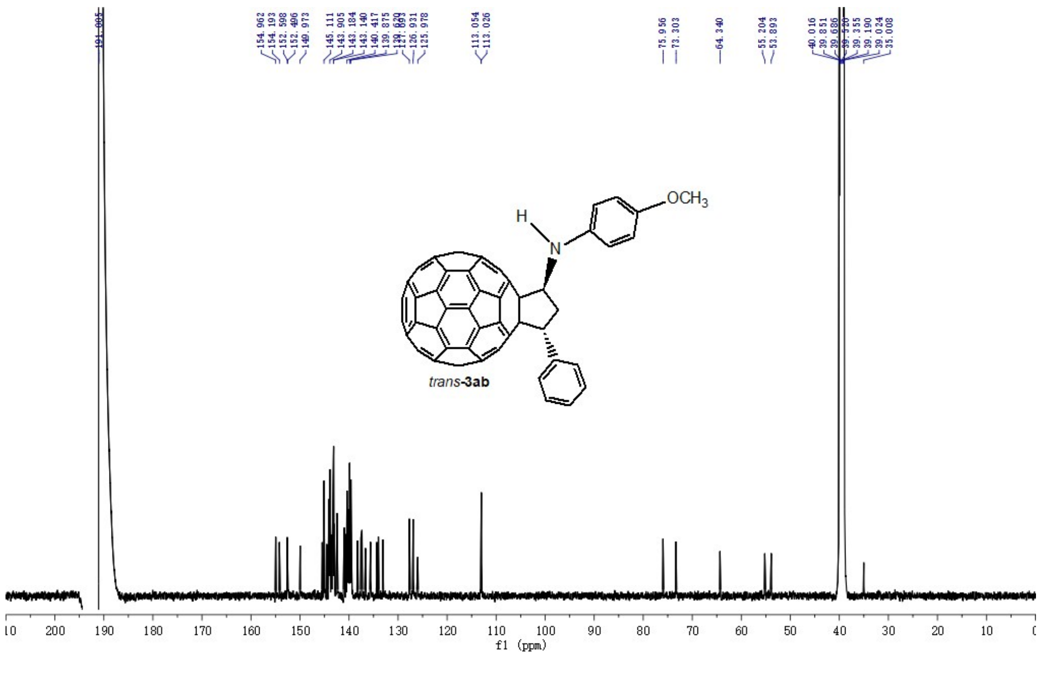

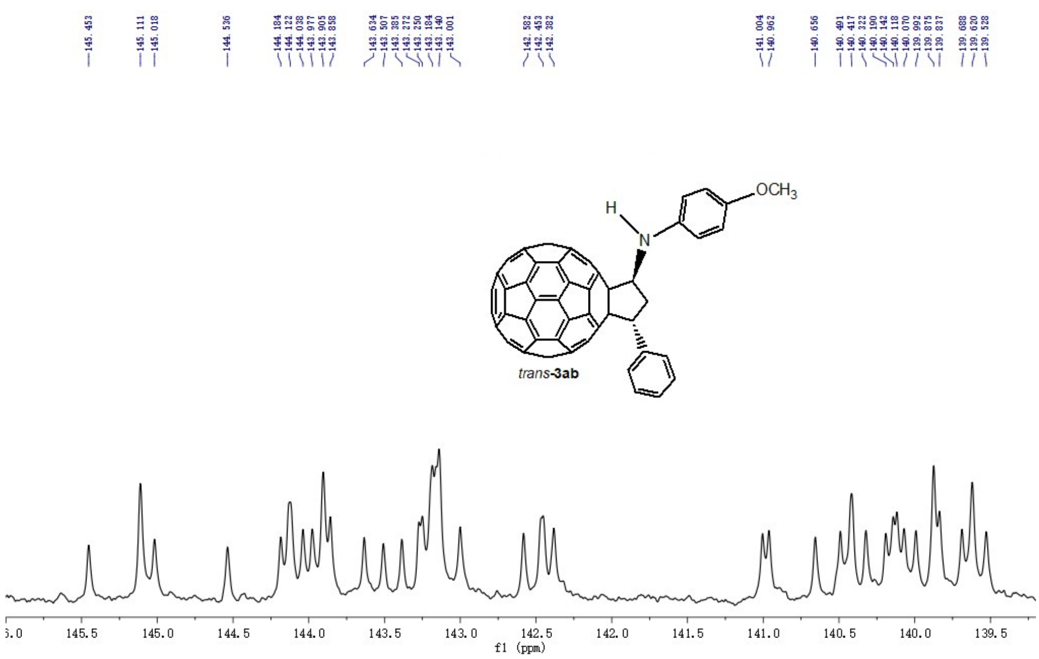

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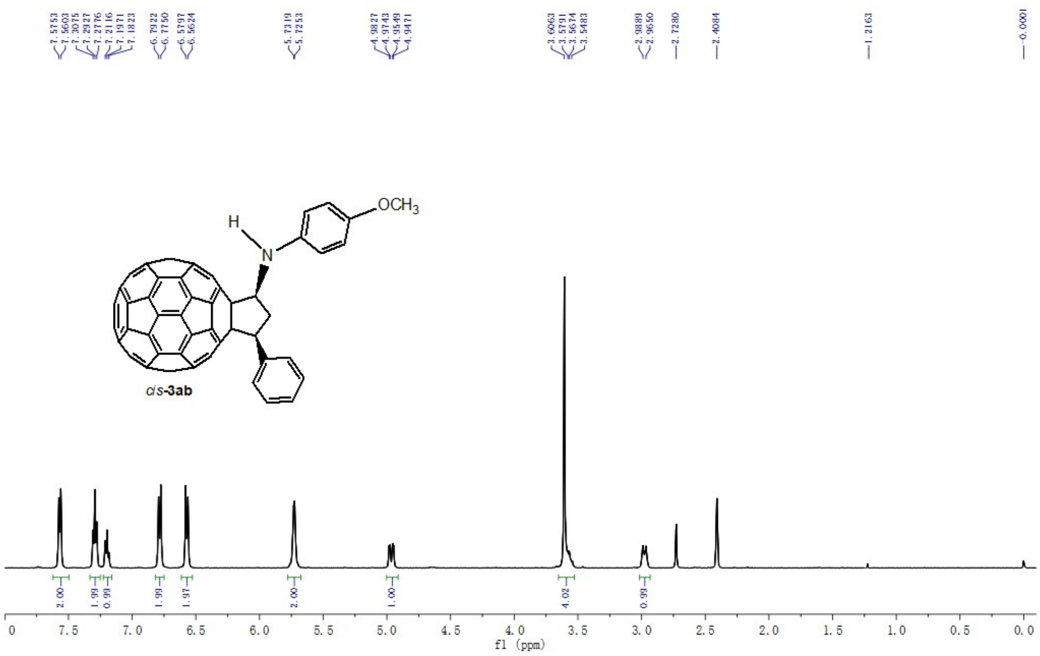

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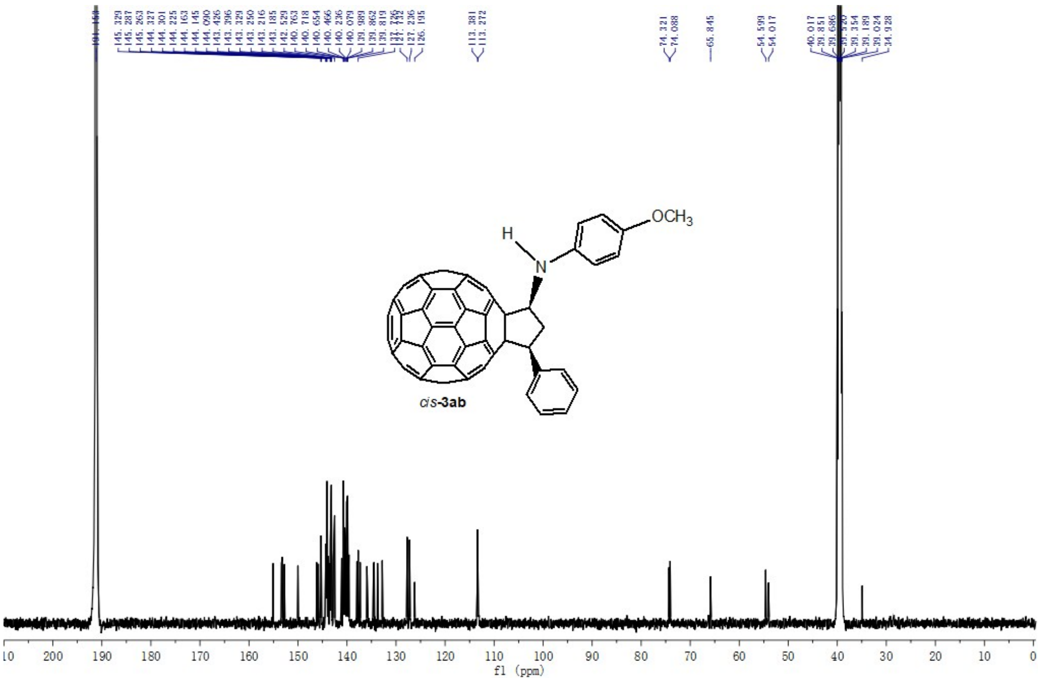
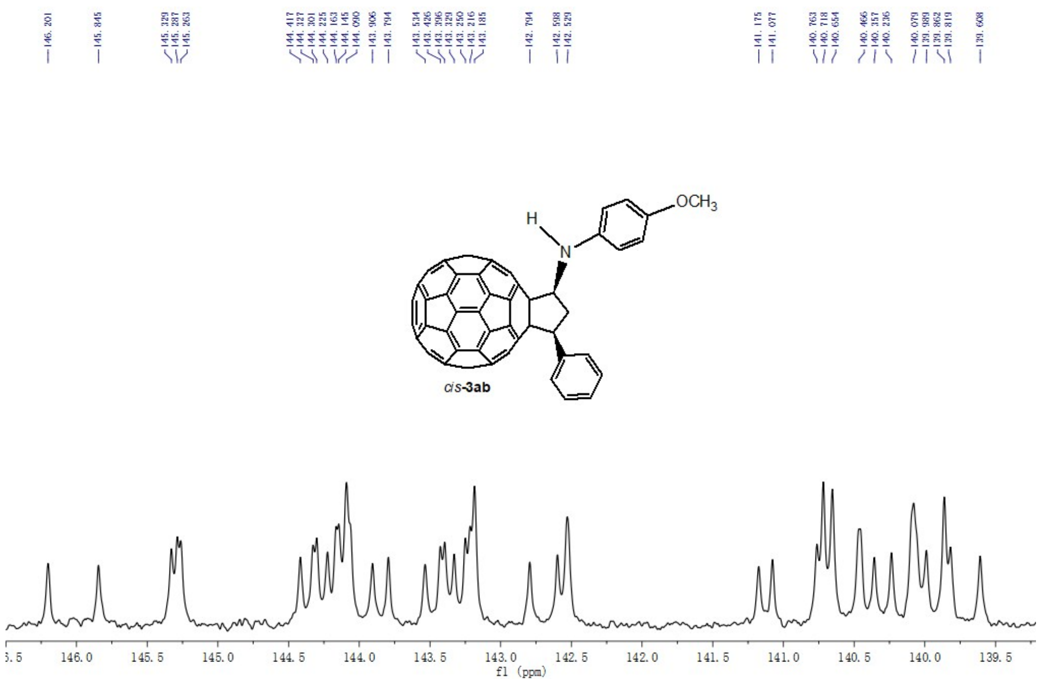
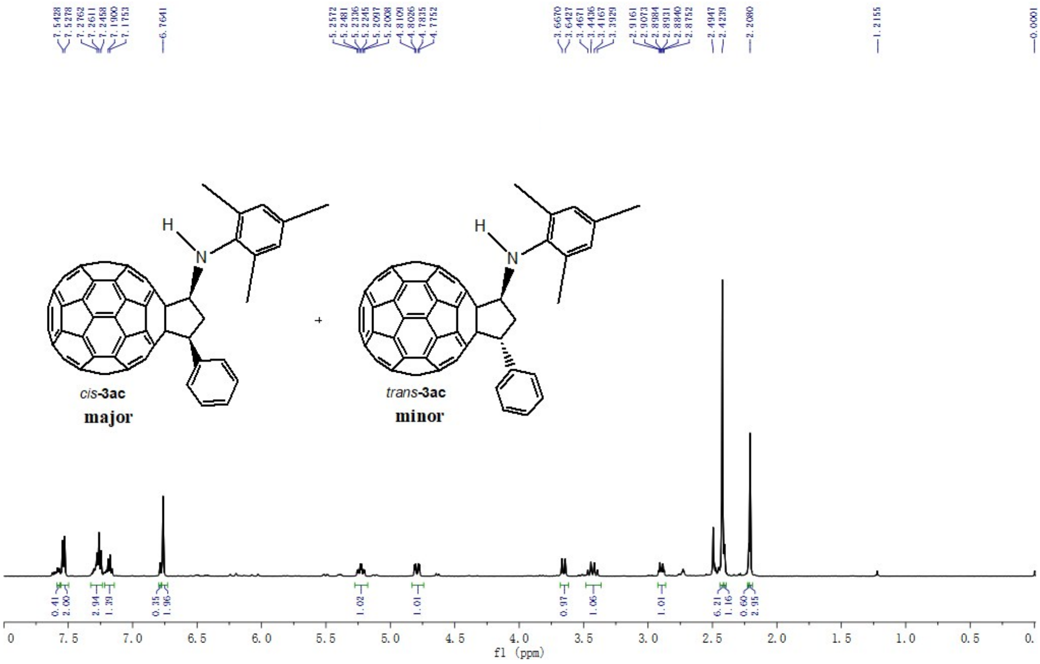
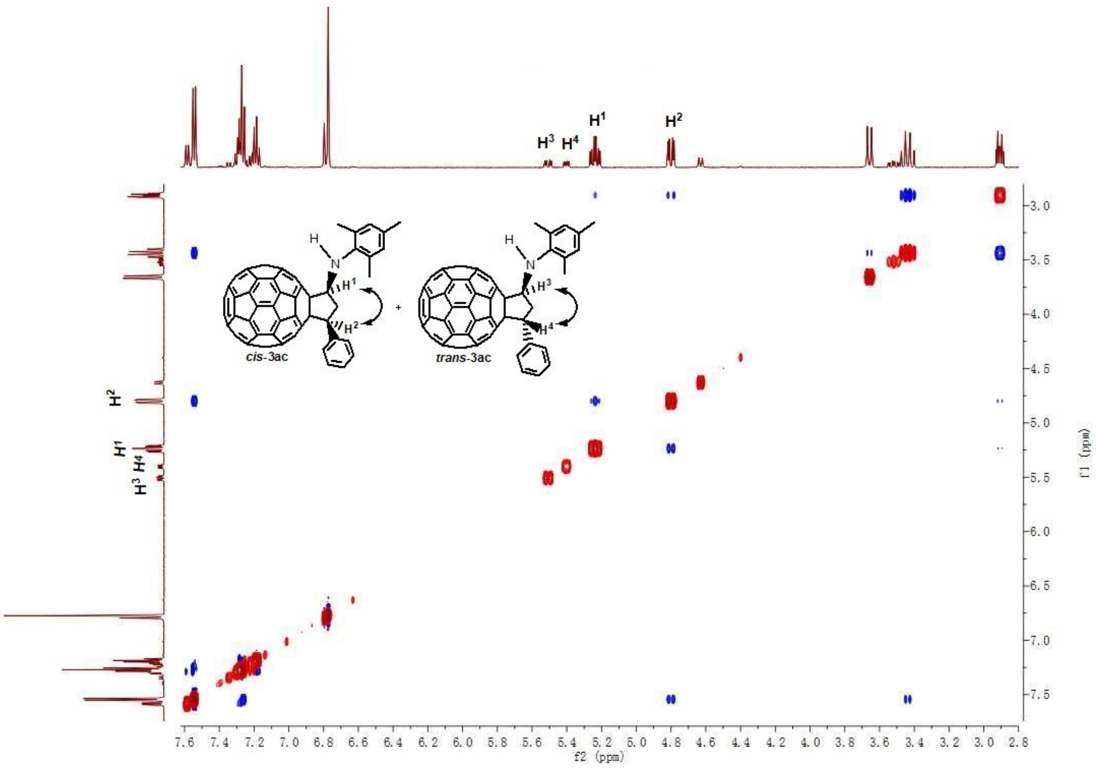




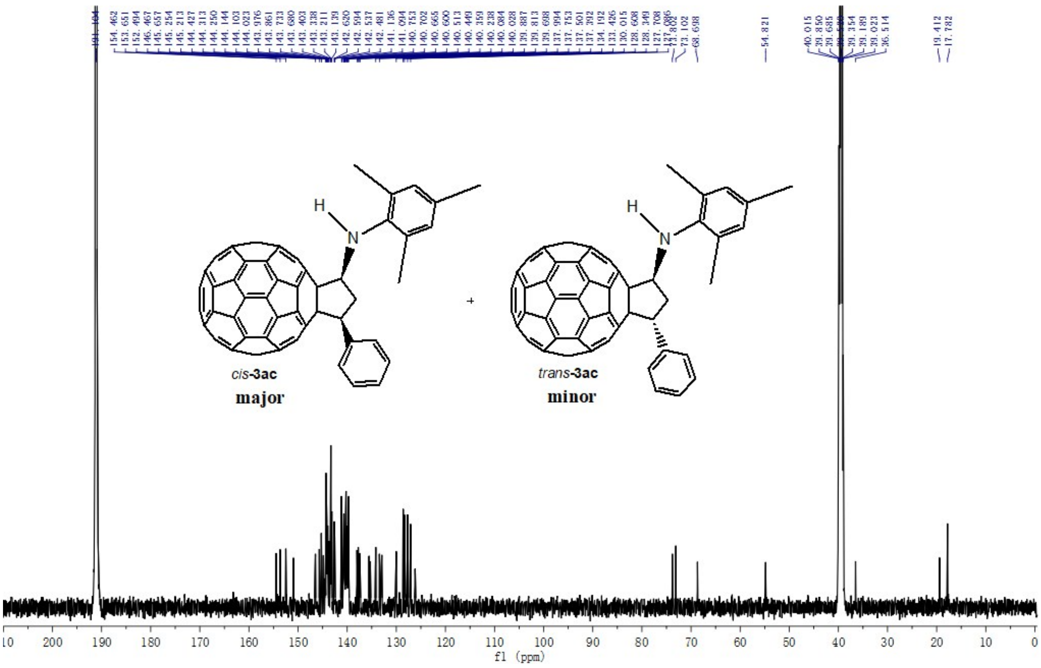
^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans/cis*-**3ac**

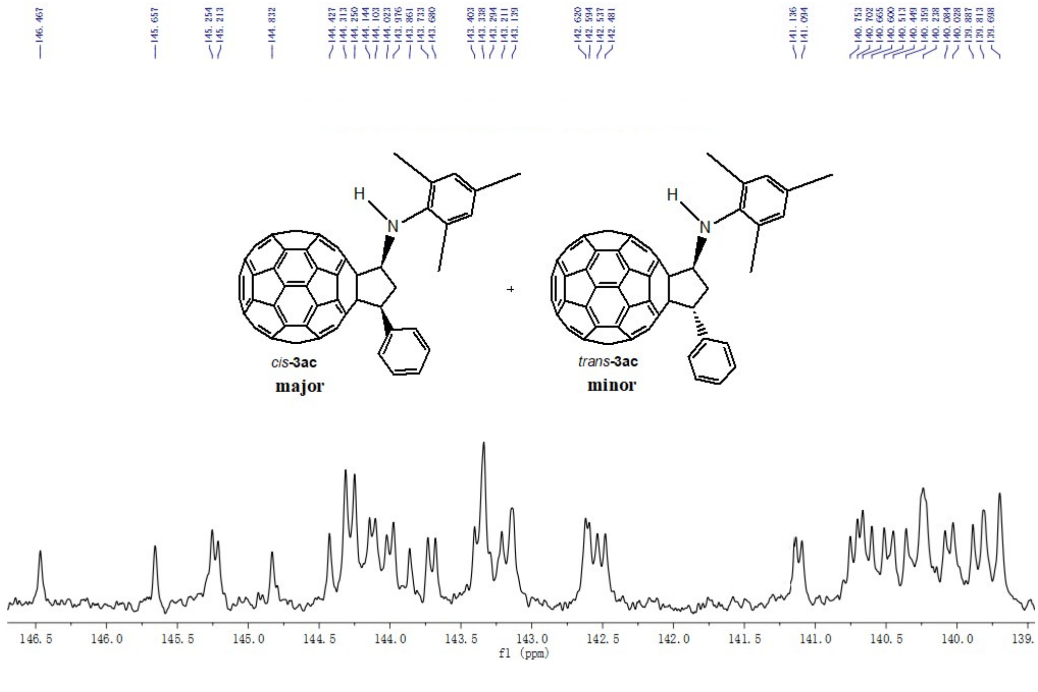


NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *trans/cis*-**3ac**

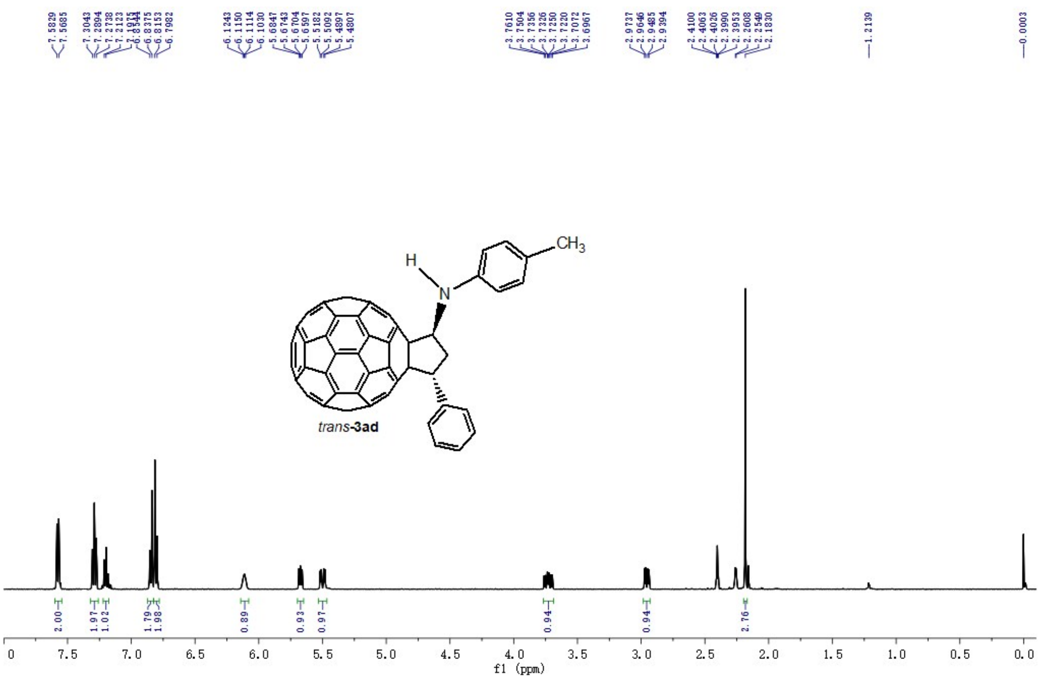


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans/cis*-**3ac**

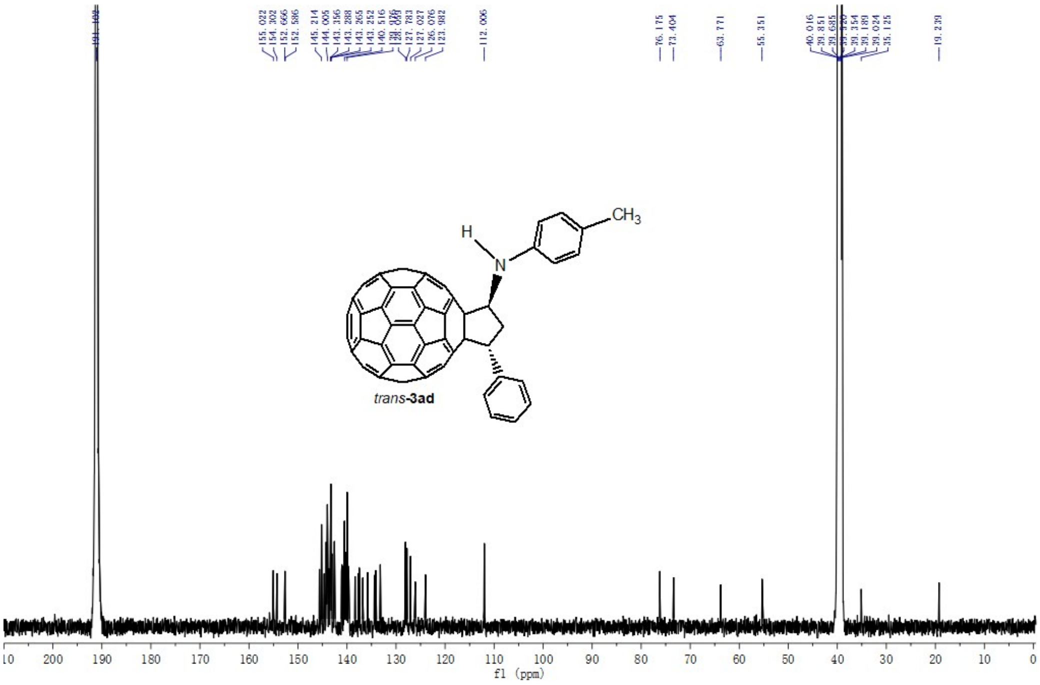


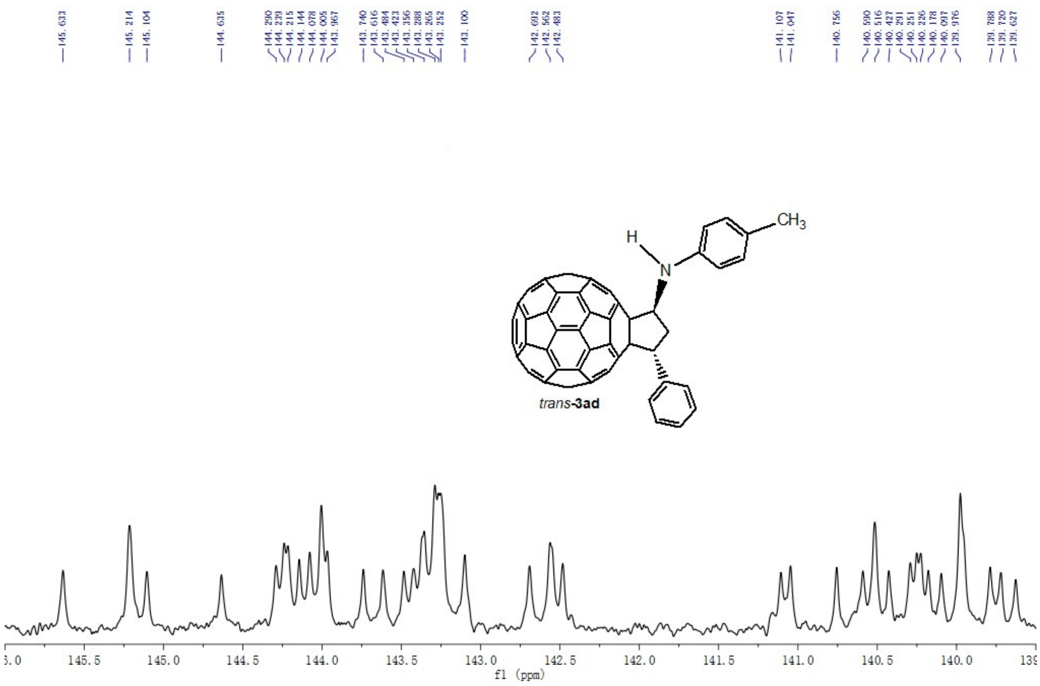


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ad**

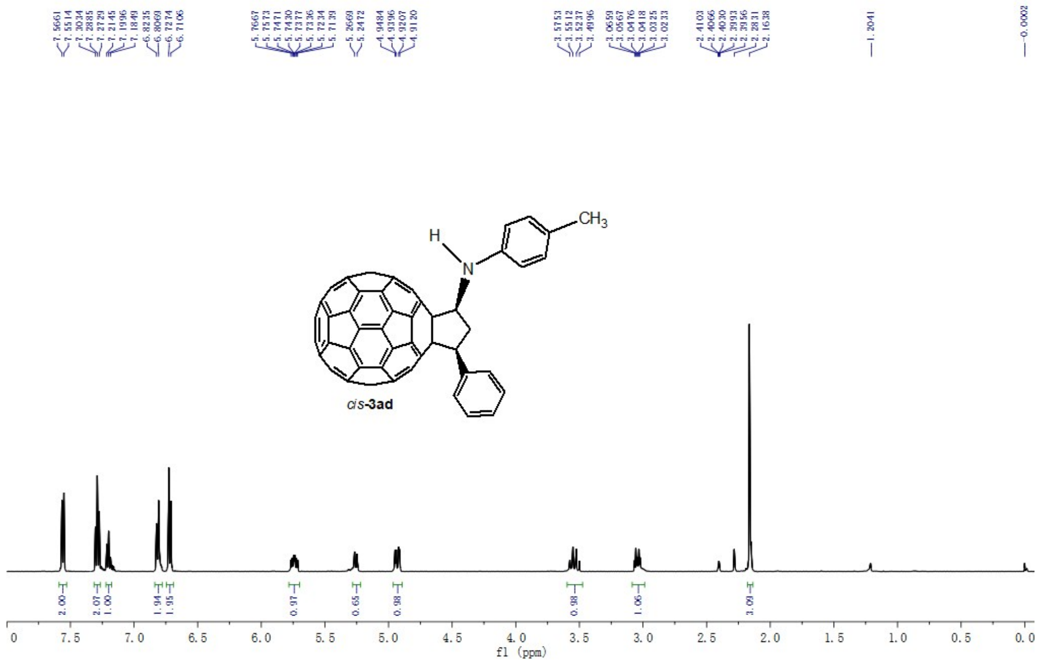


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ad**

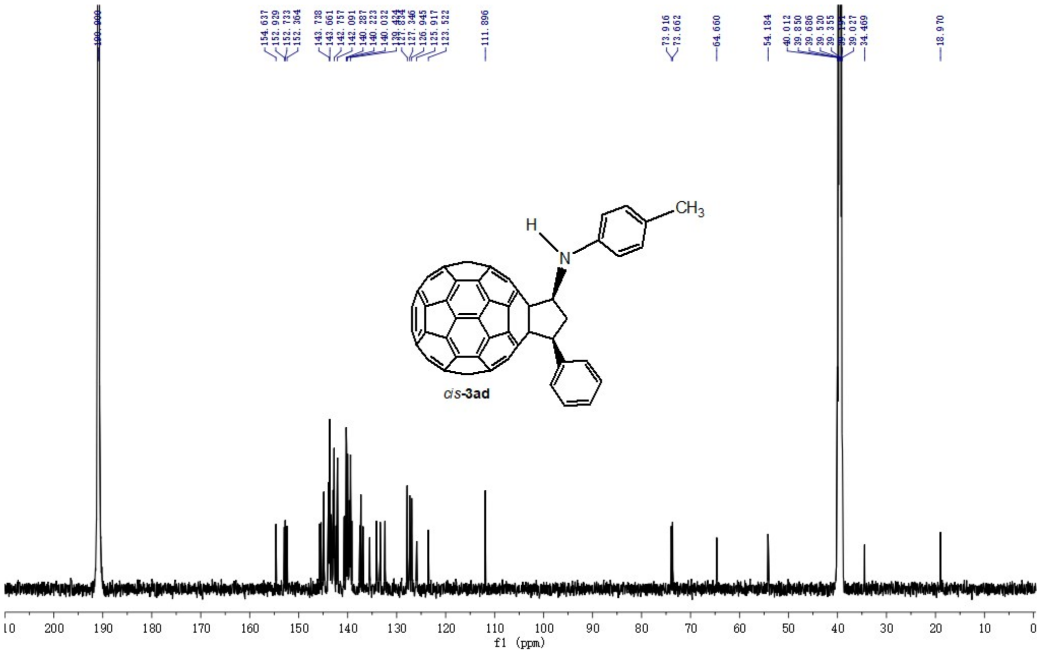


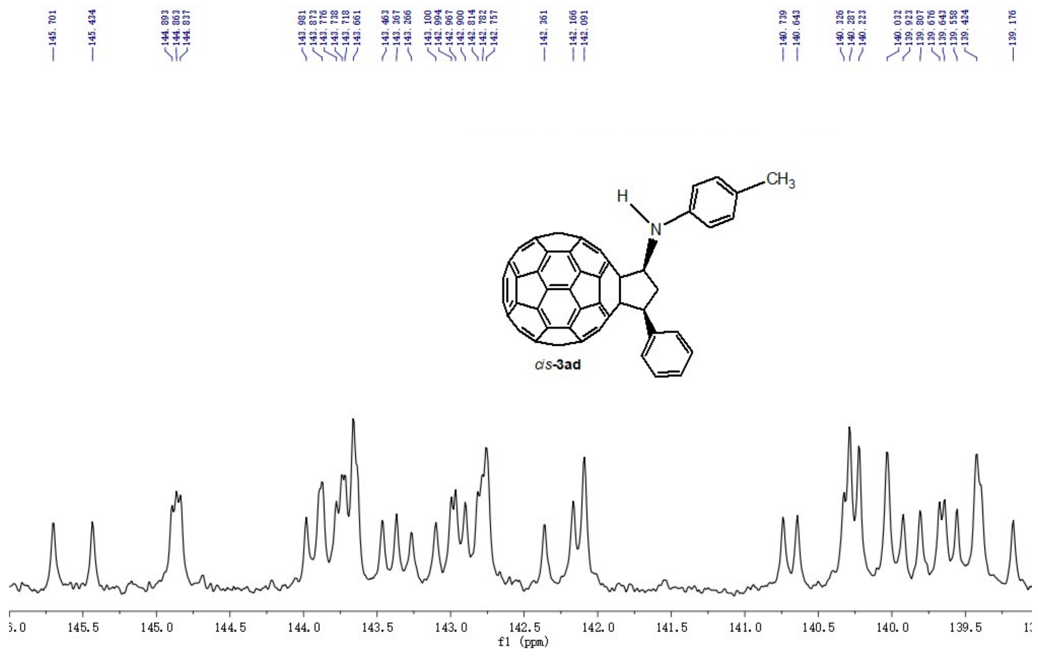


^1H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3ad**

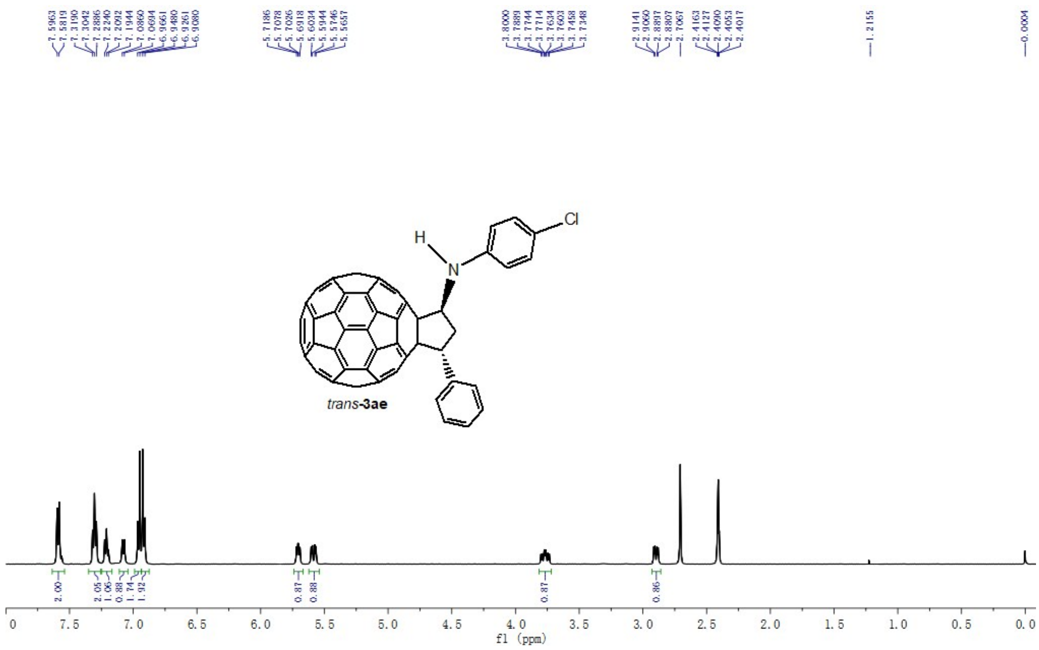


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3ad**

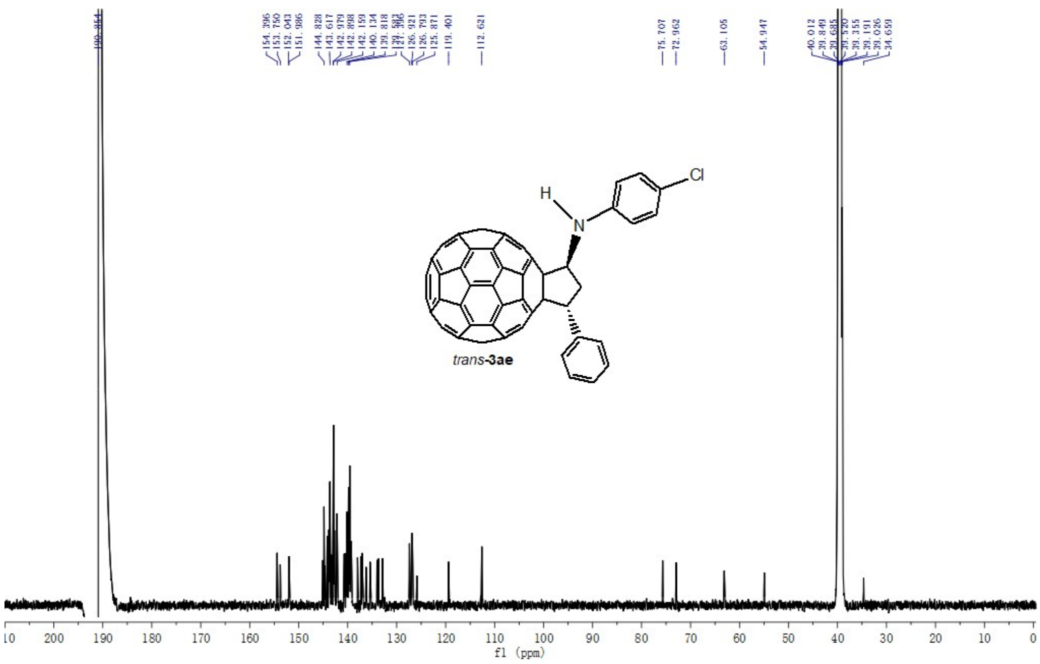


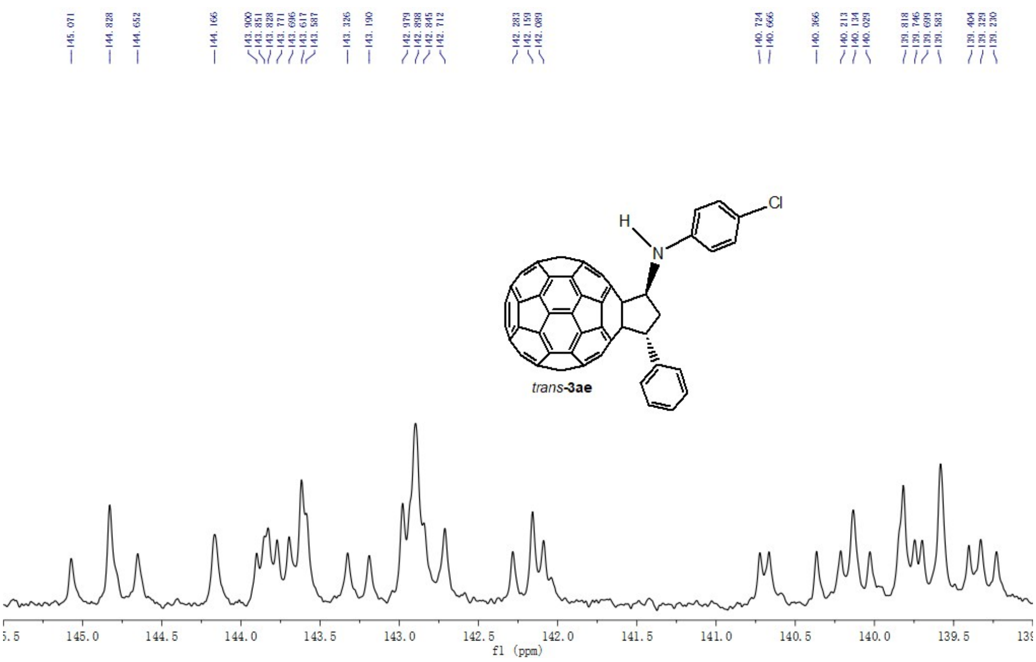


[1]H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ae**



[13]C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ae**





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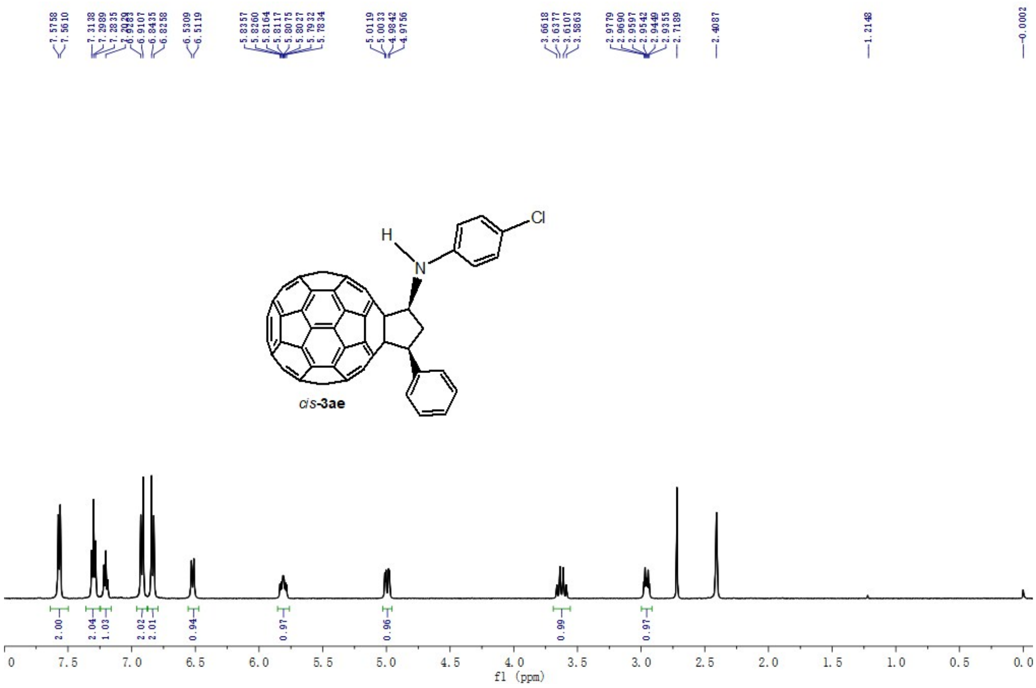

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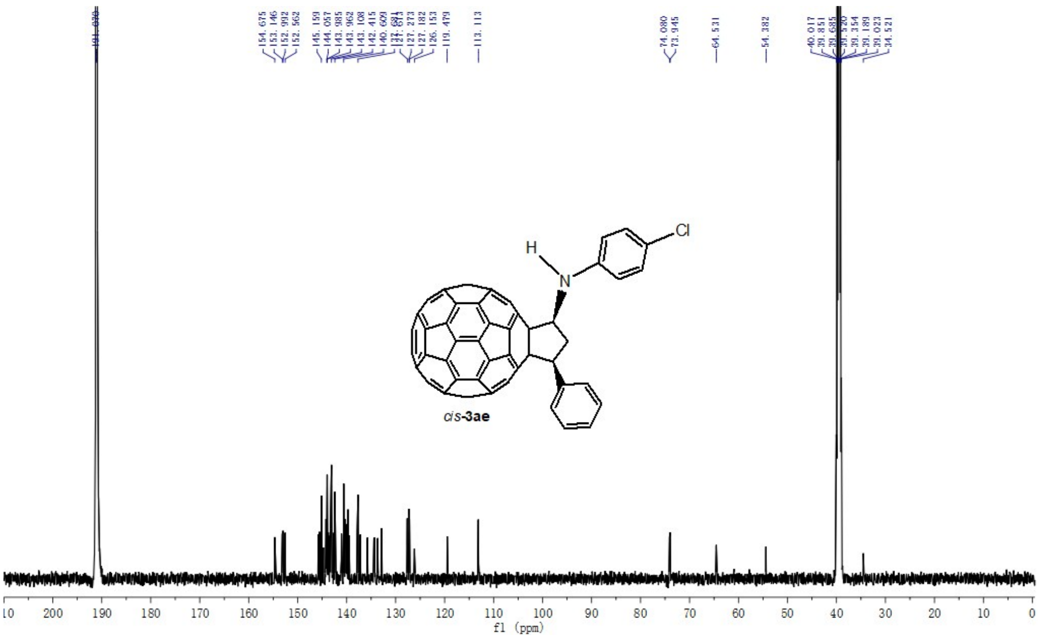
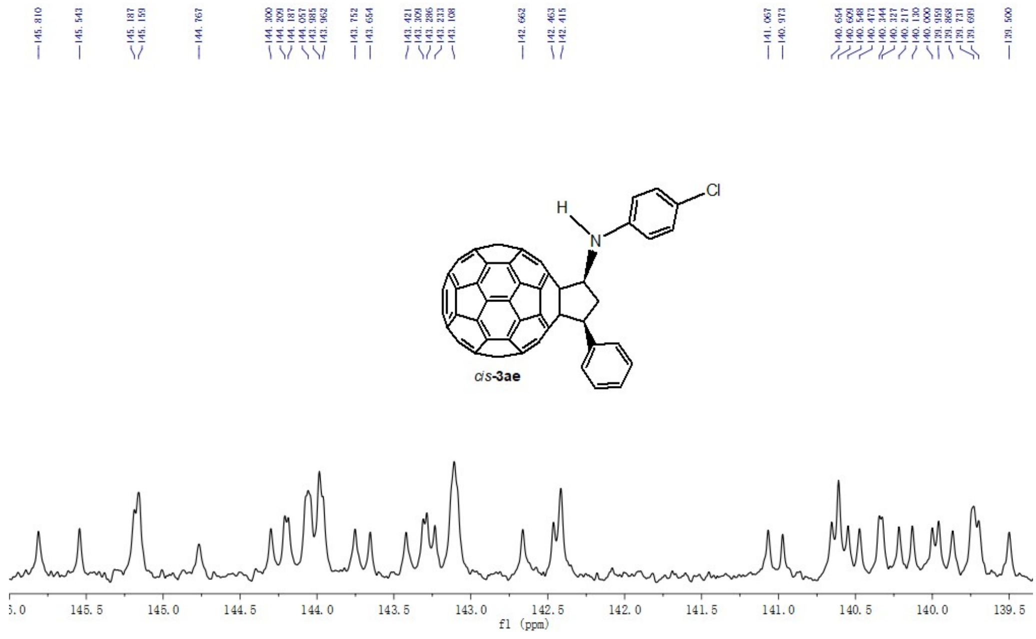
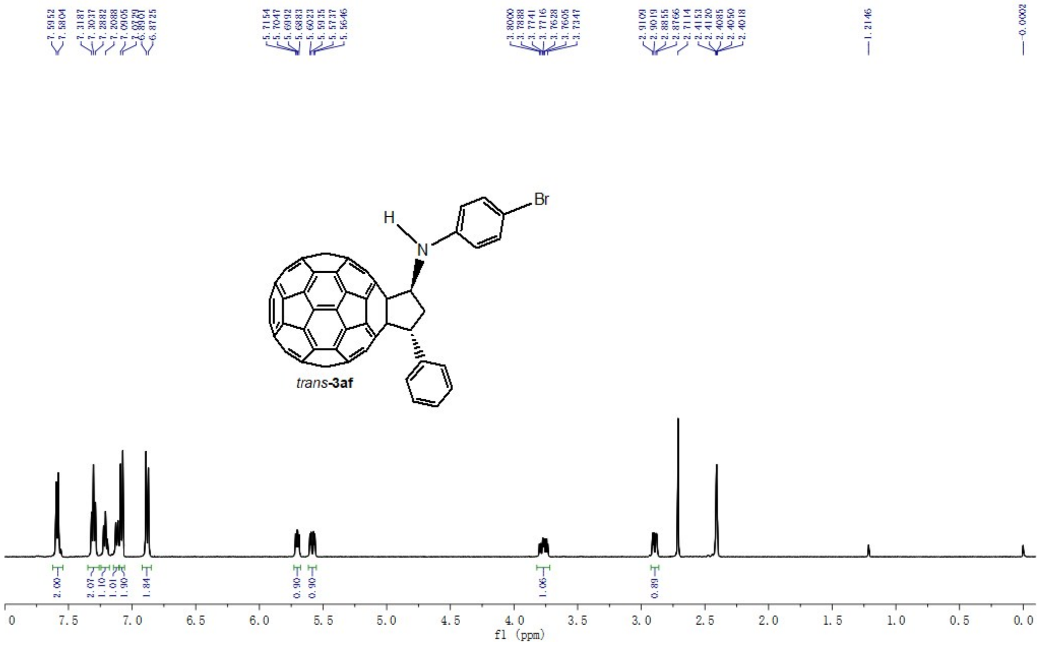
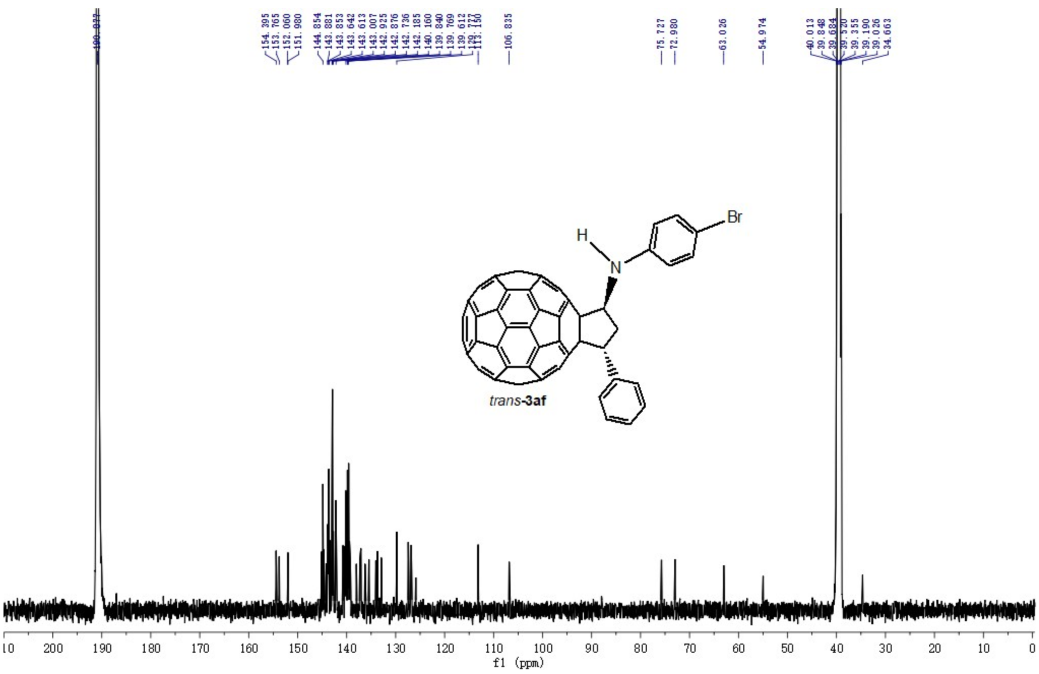


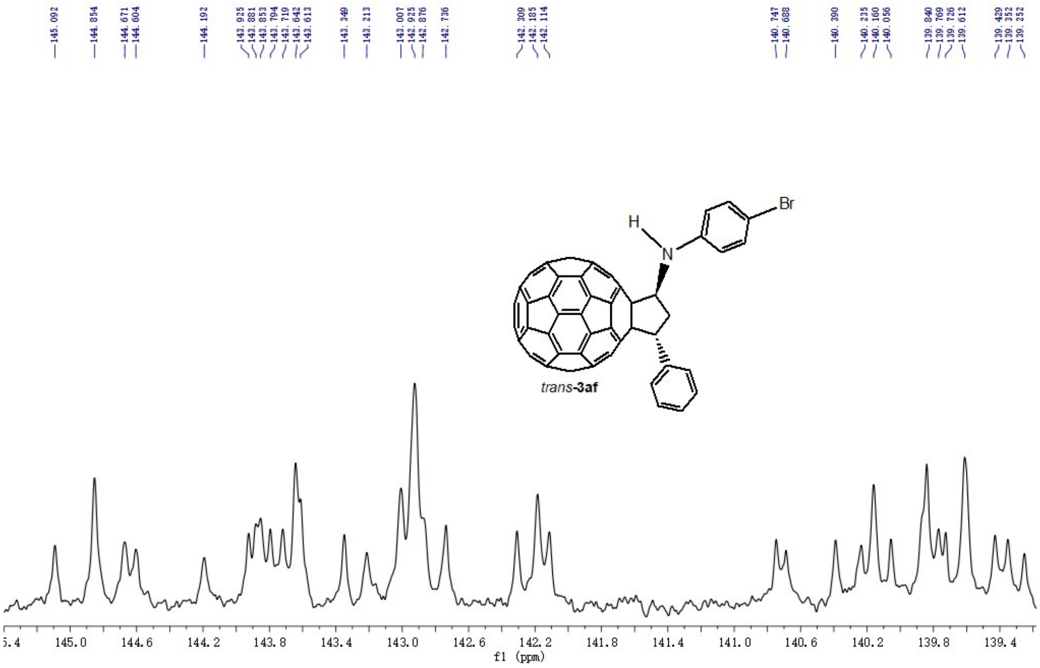


^1H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3af**

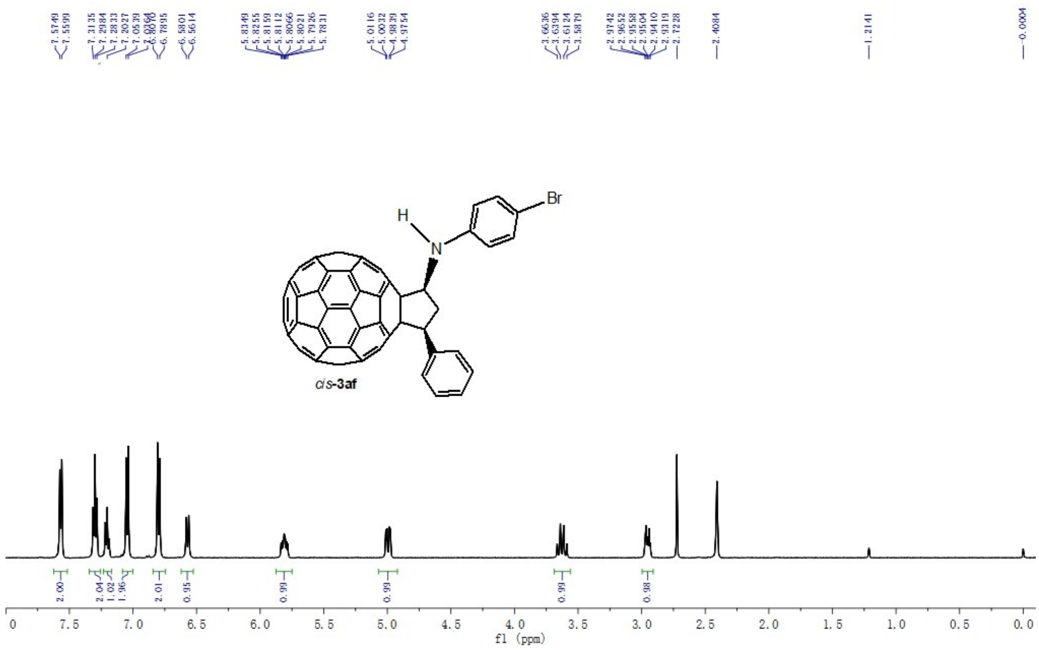


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3af**

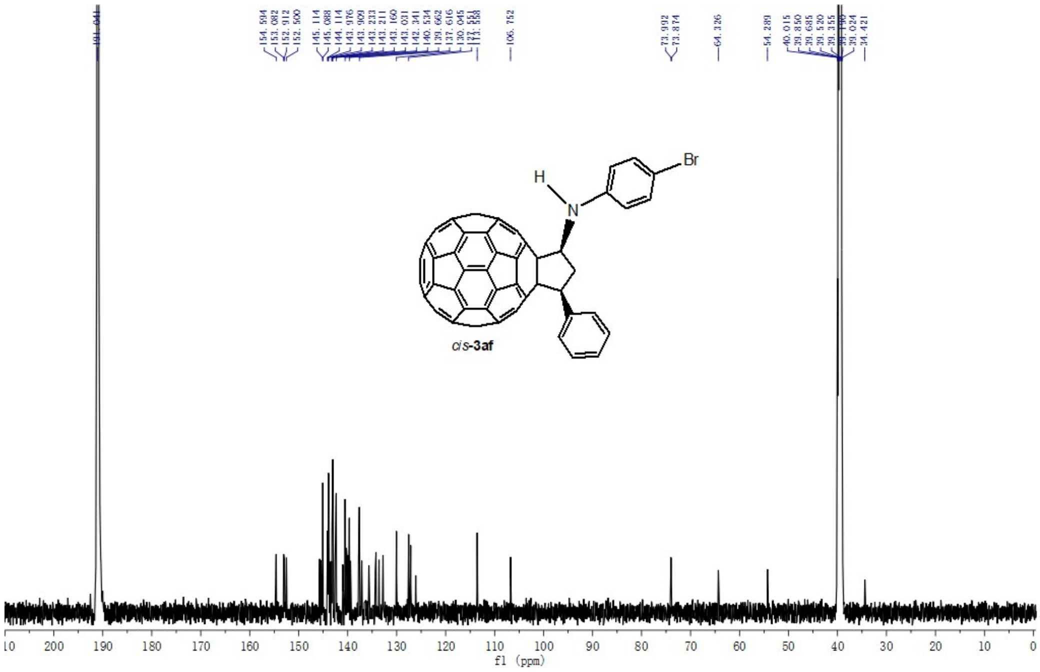


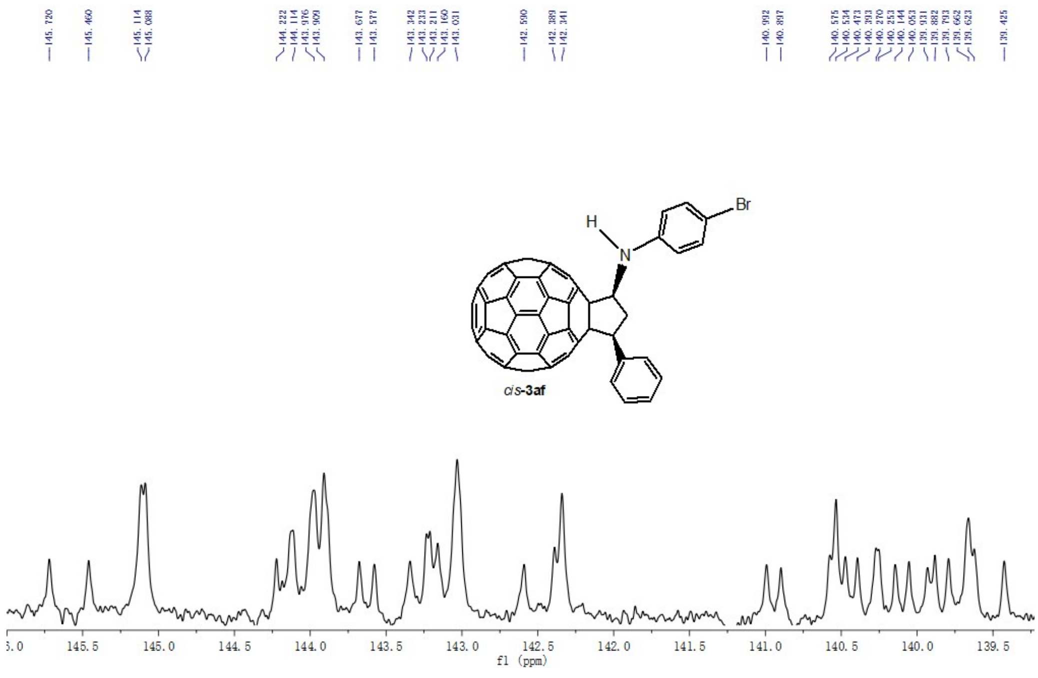


^1H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3af**

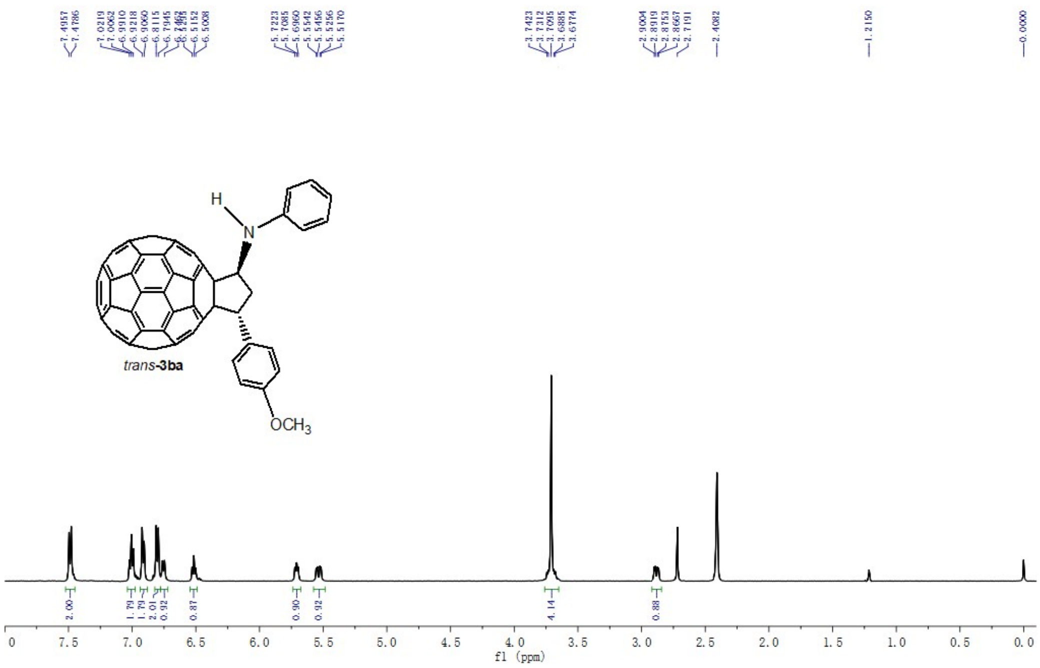


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3af**





^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ba**



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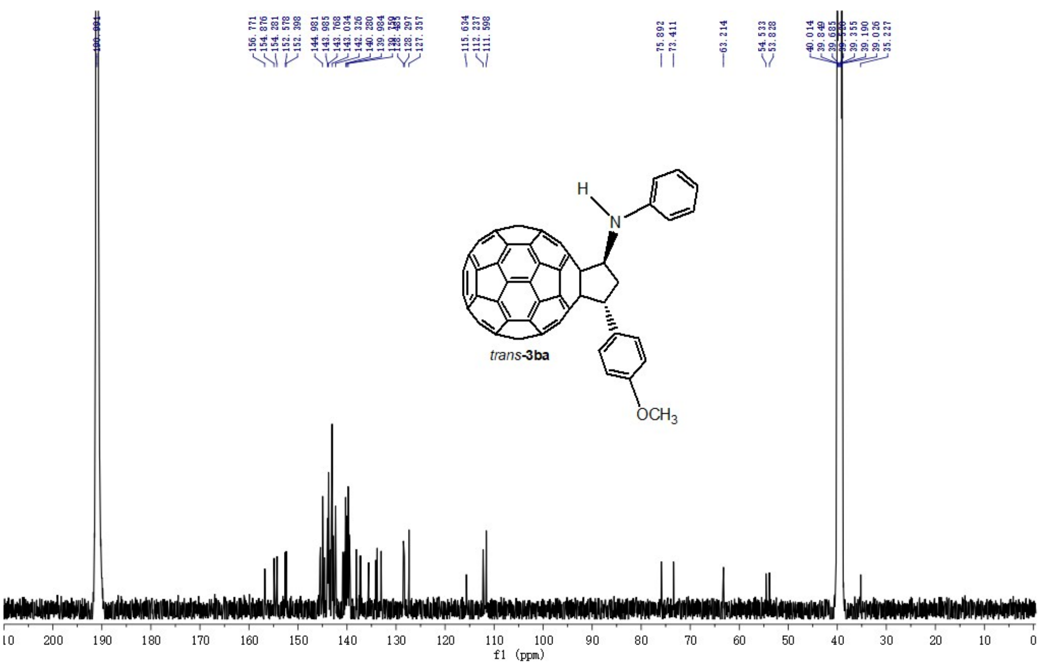
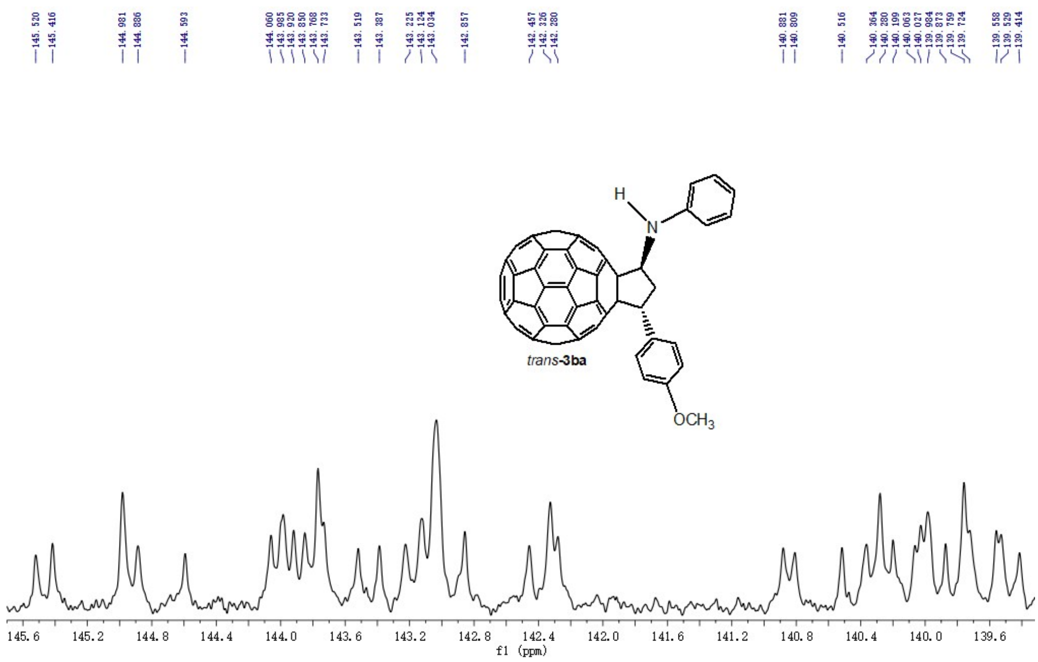
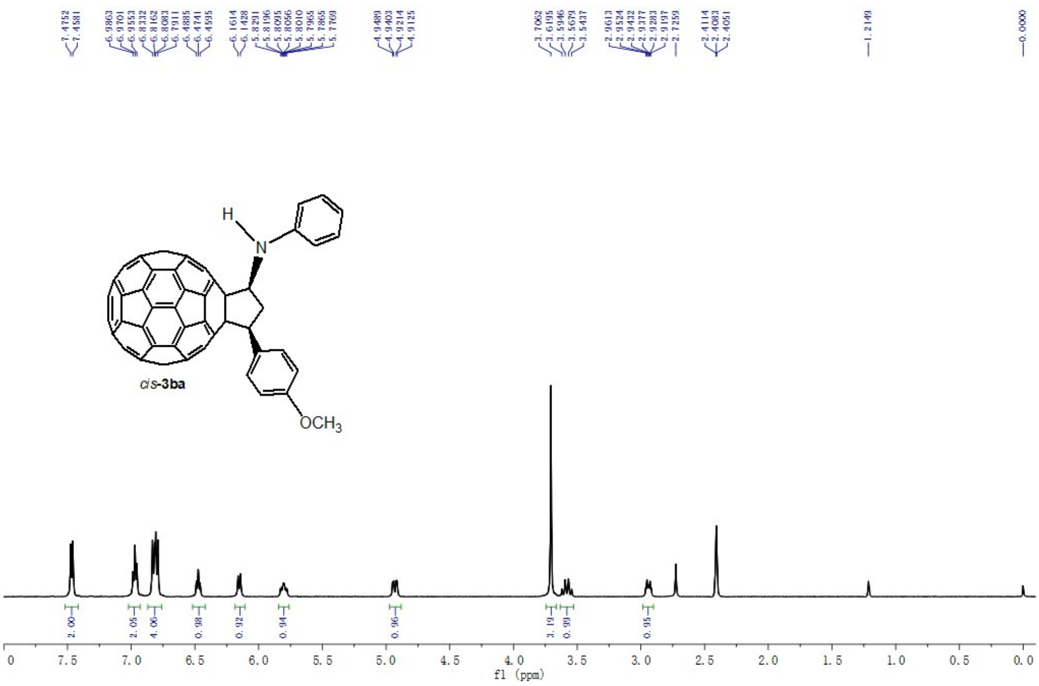
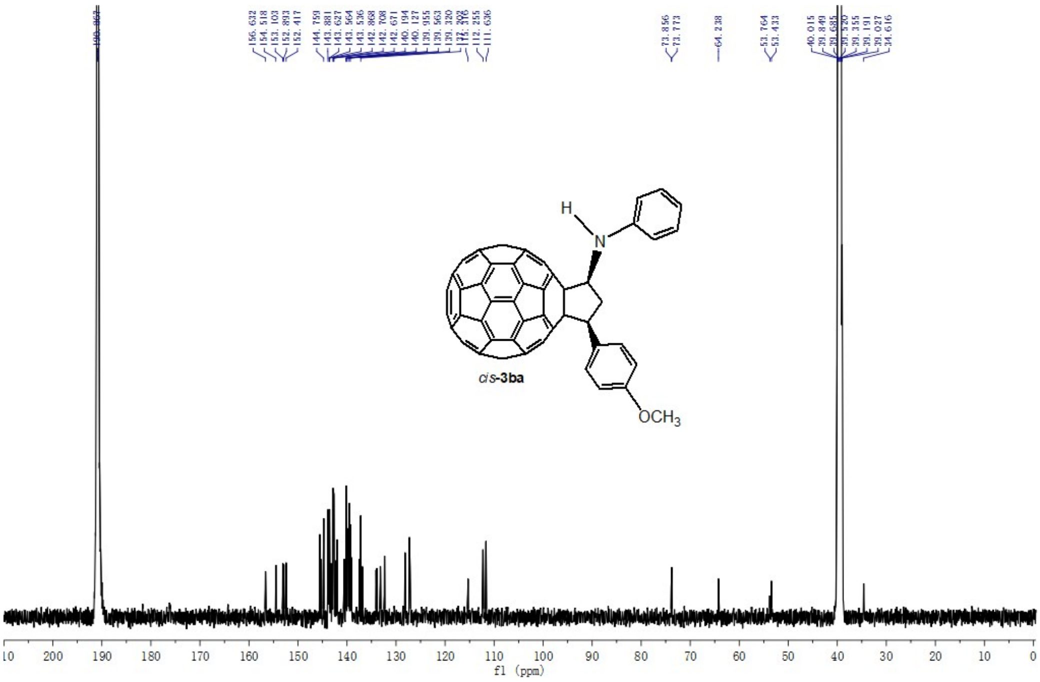


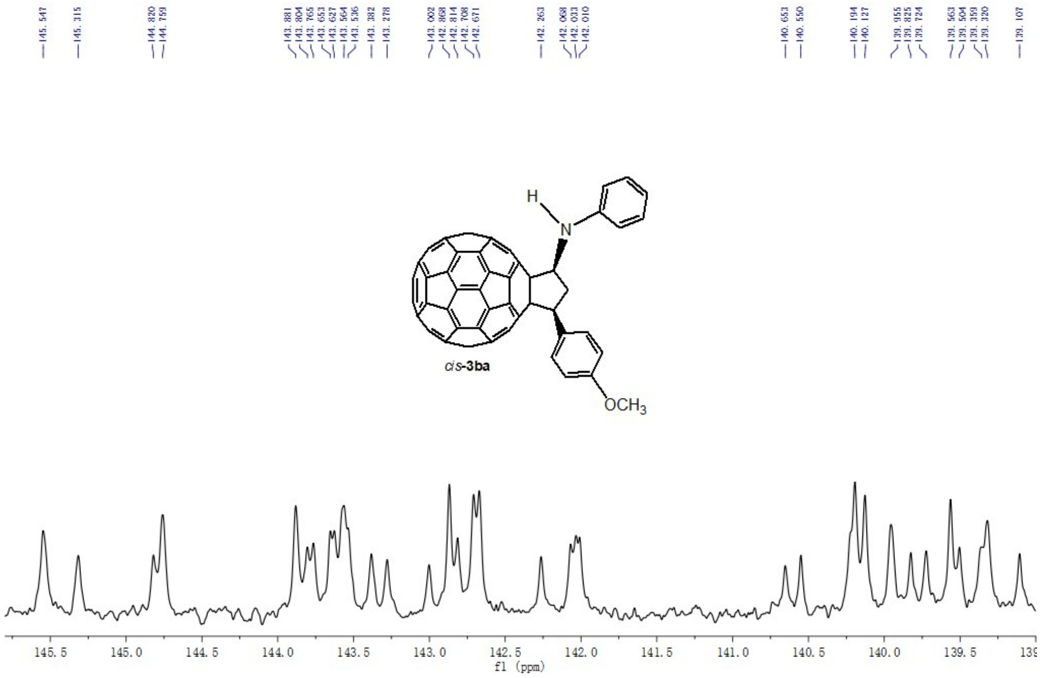


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3ba**

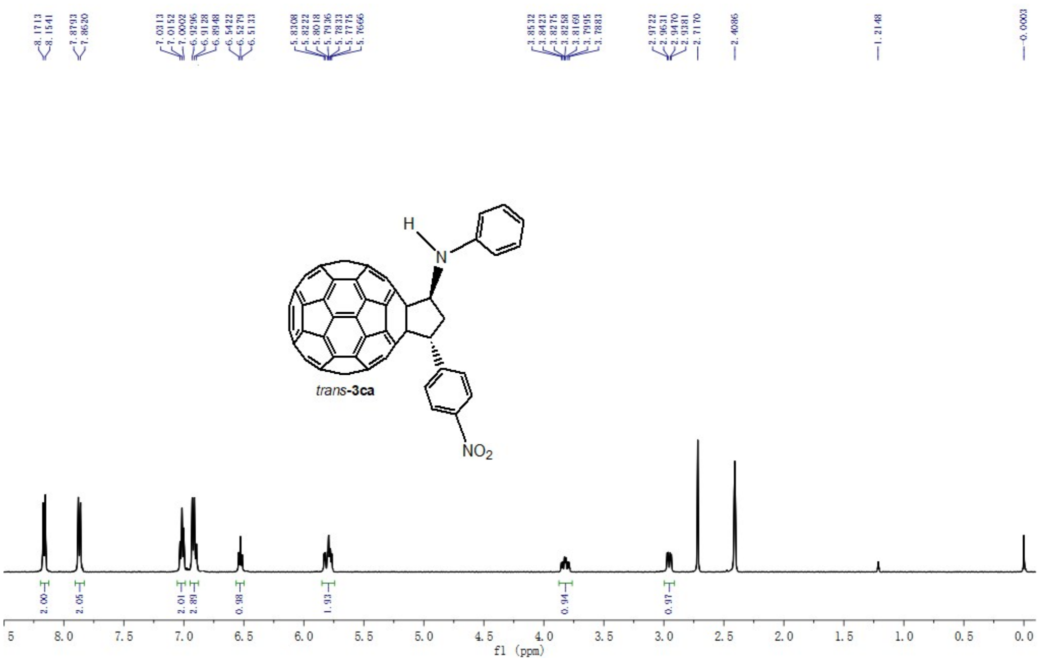


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**3ba**

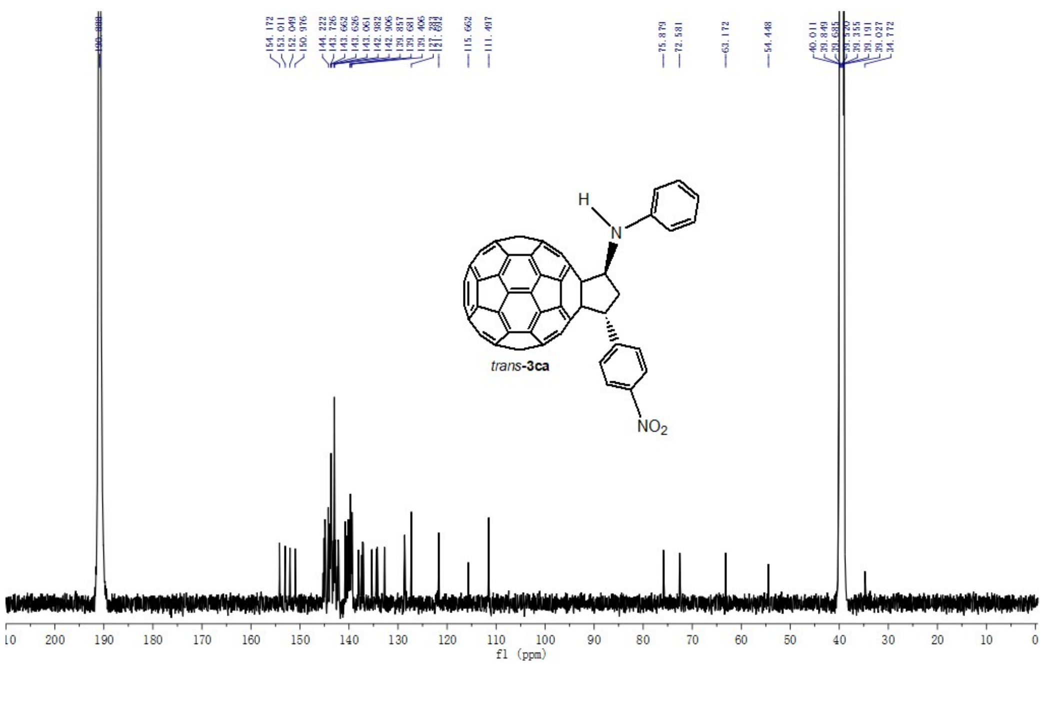


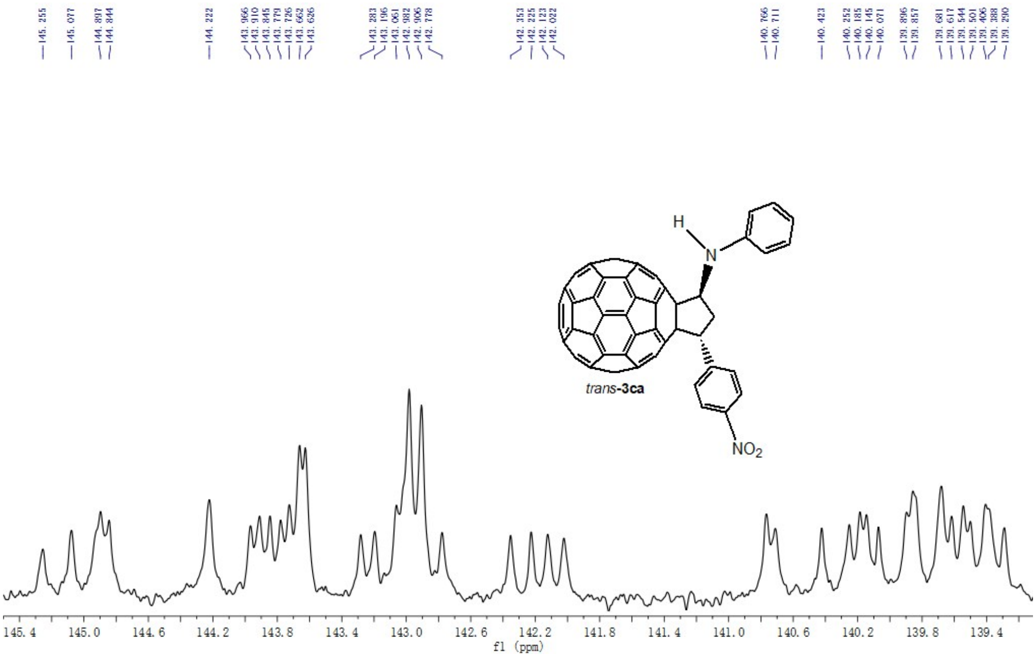


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ca**



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**3ca**





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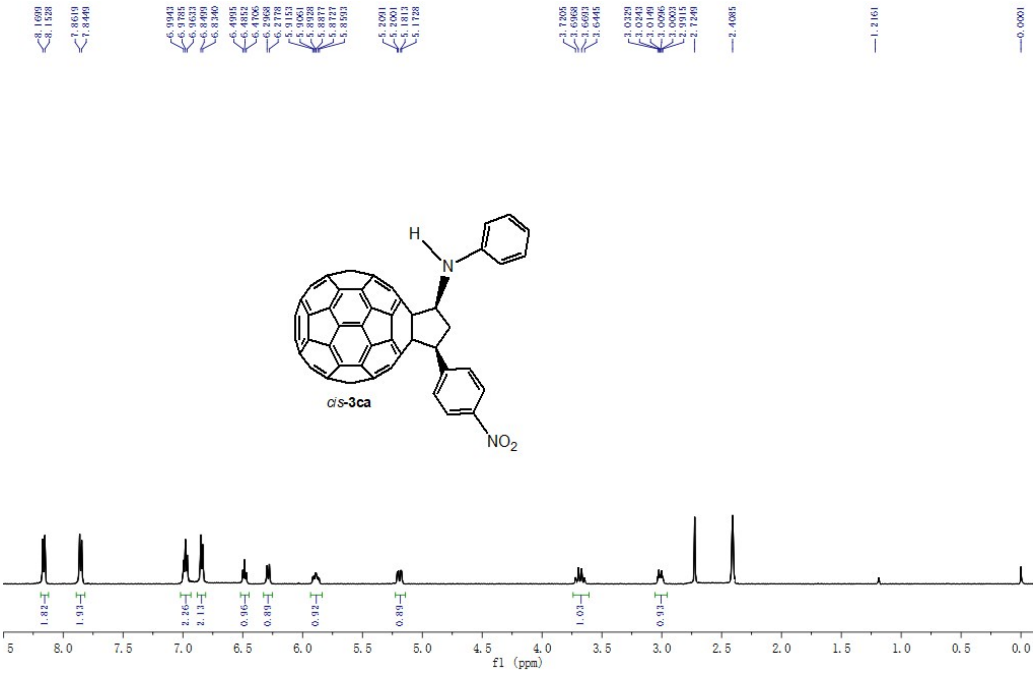

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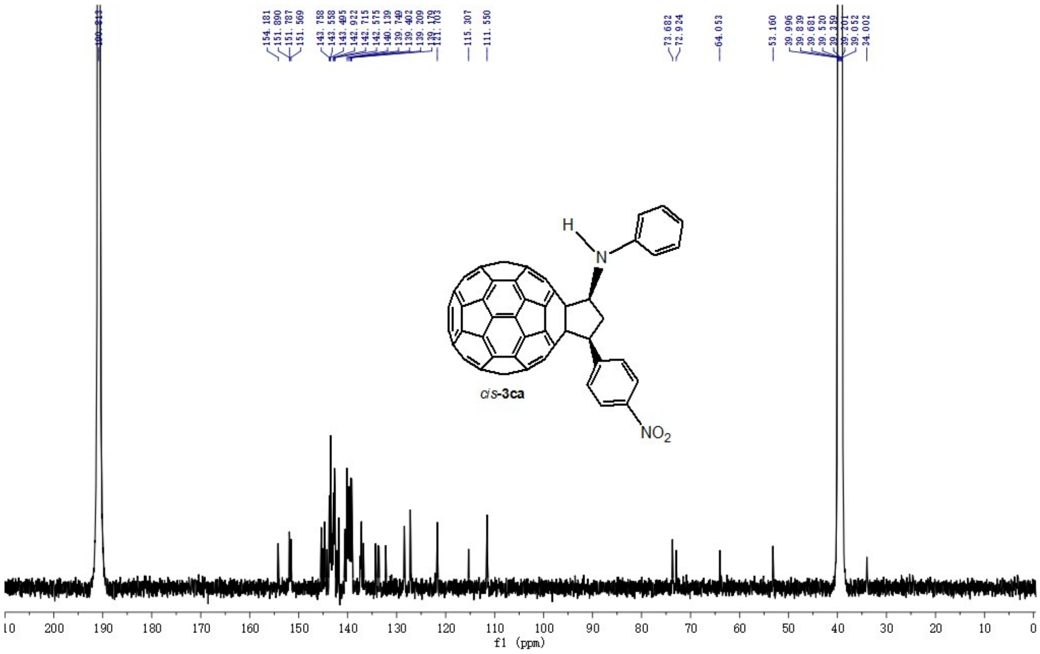
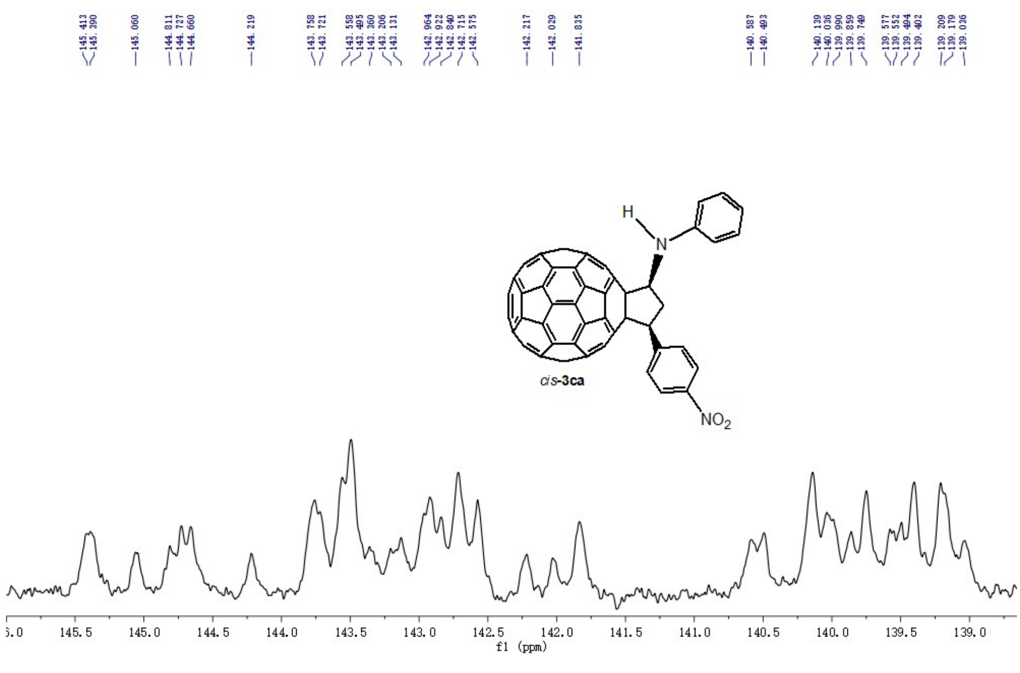
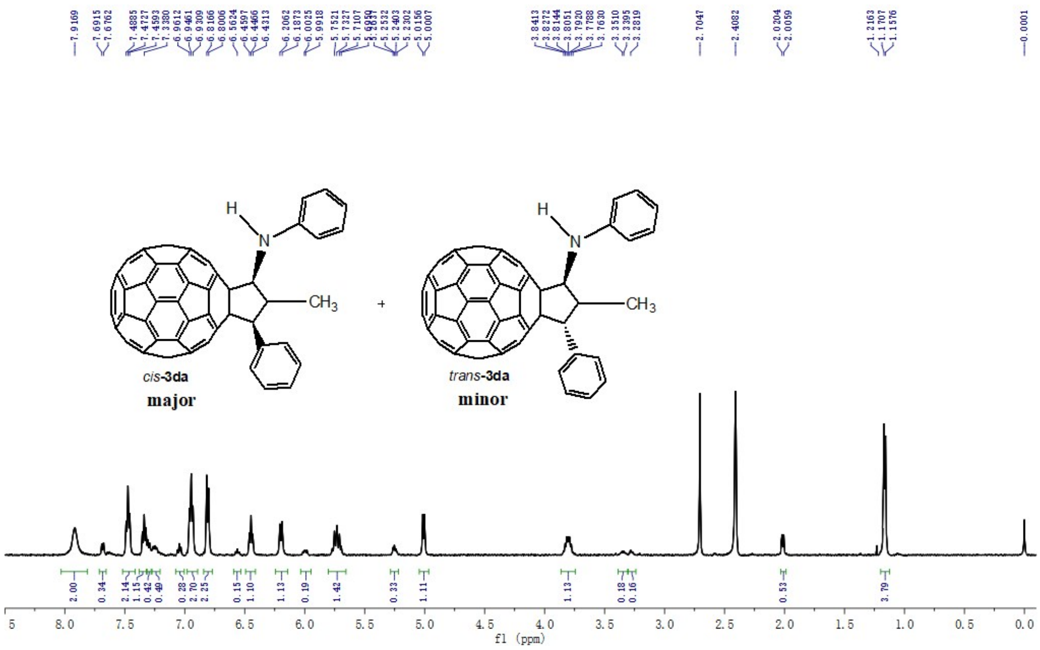
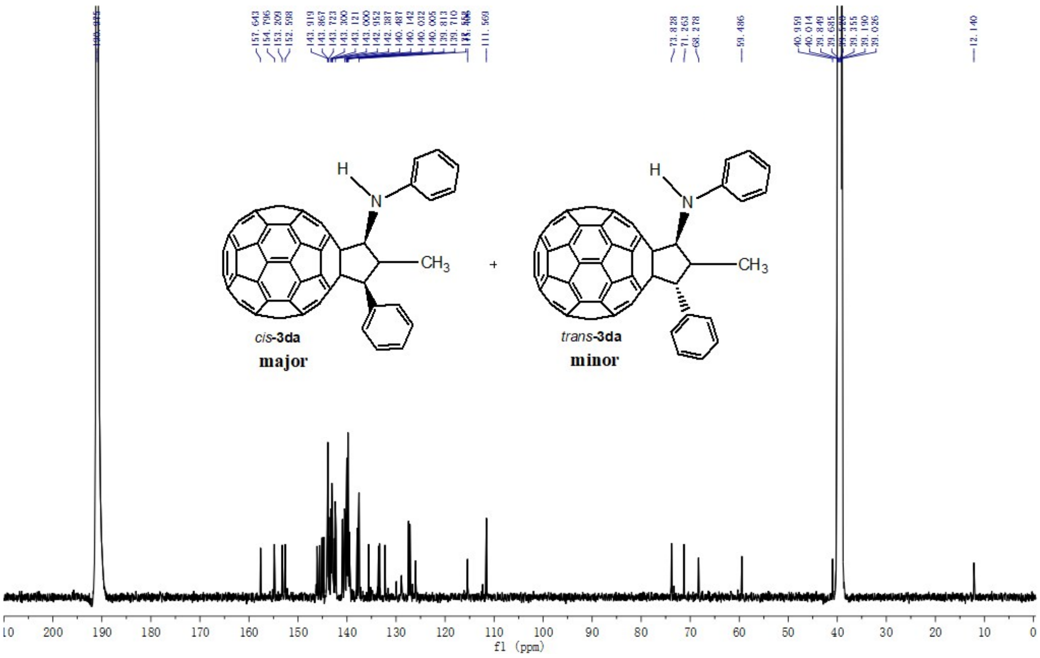


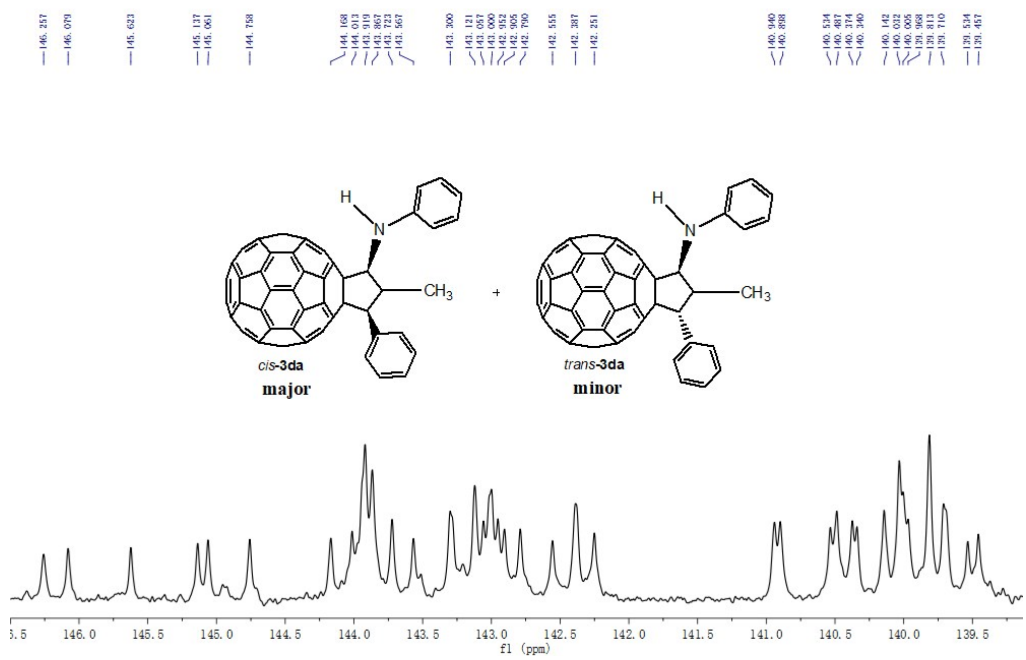


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans/cis*-**3da**

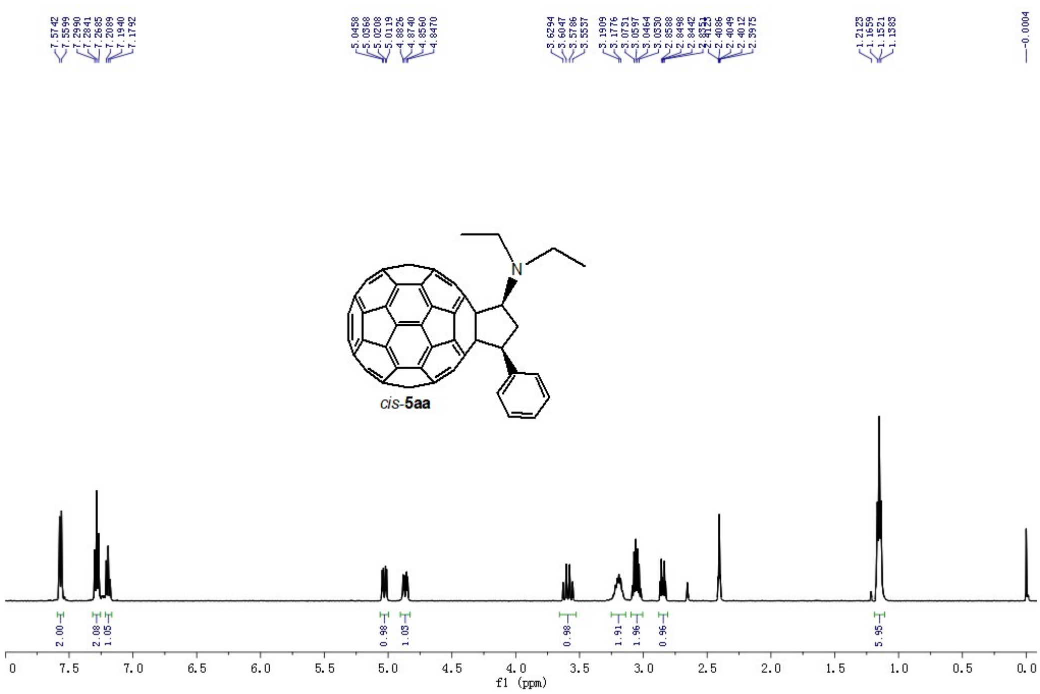


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans/cis*-**3da**

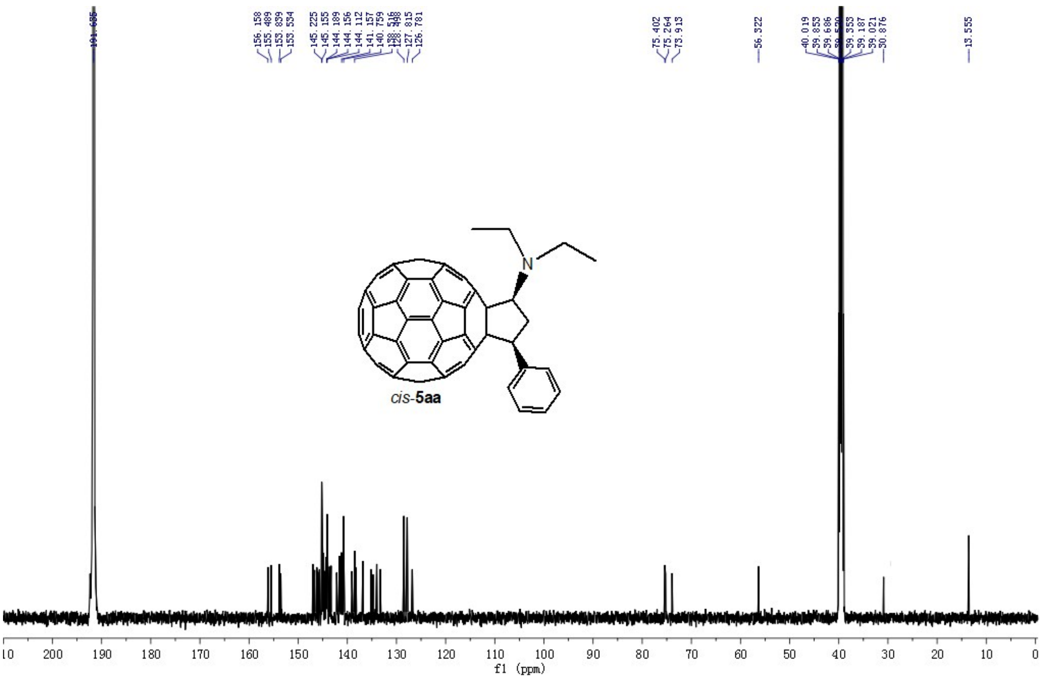


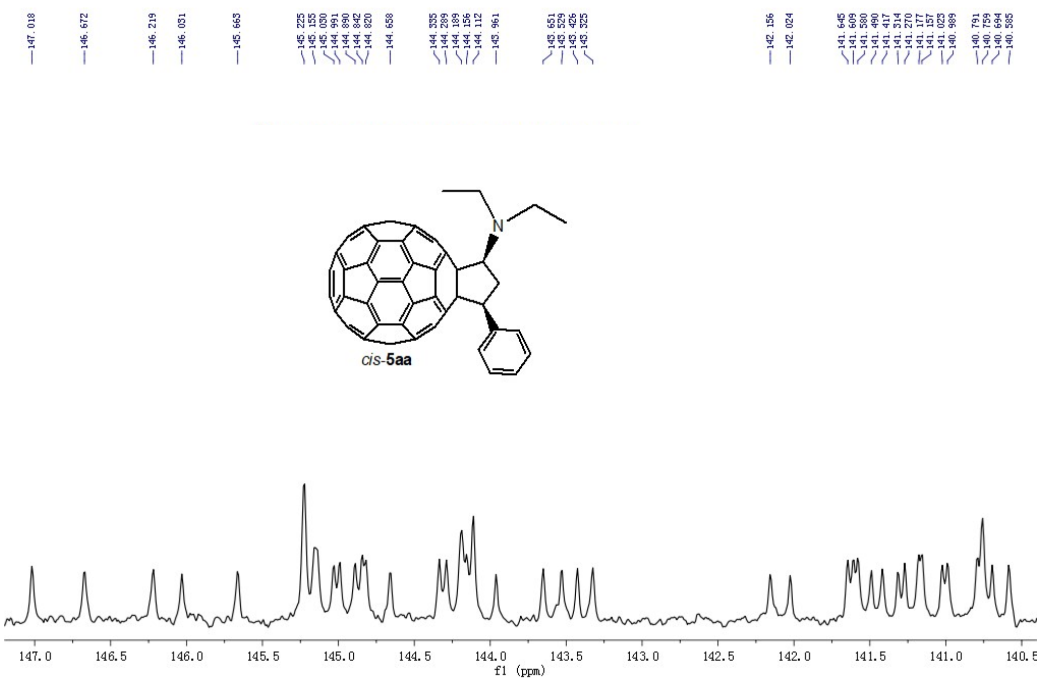


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5aa**

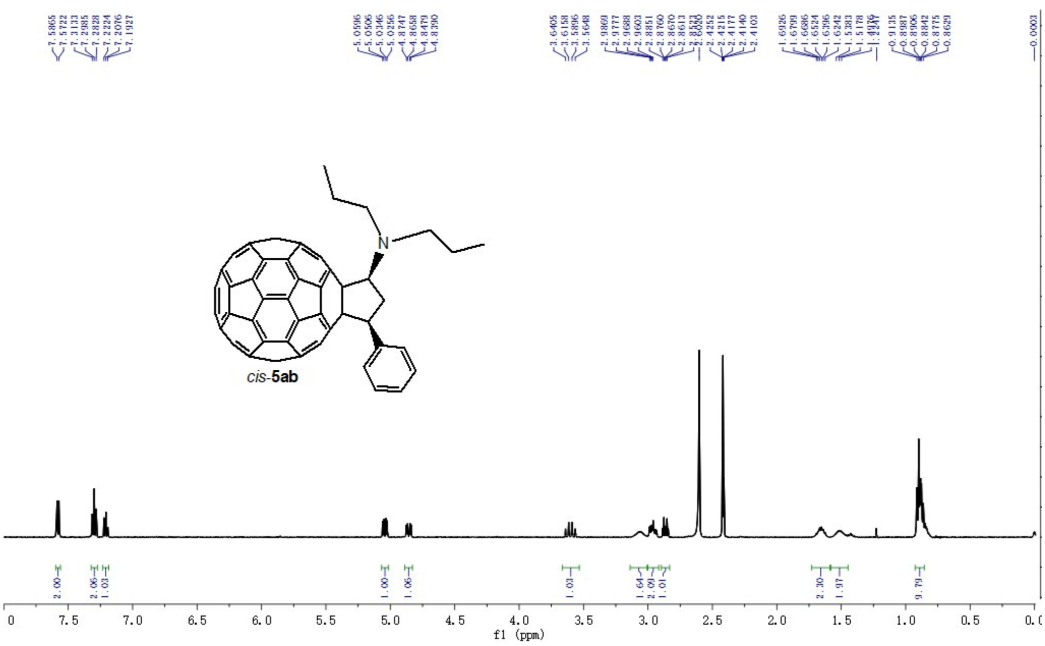


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5aa**

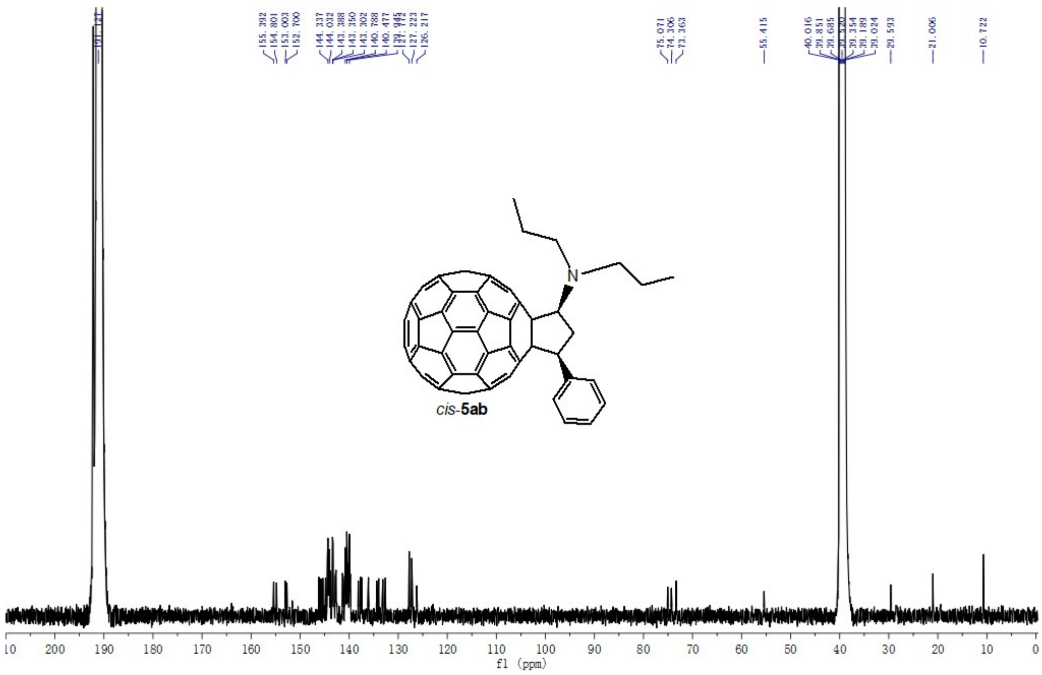


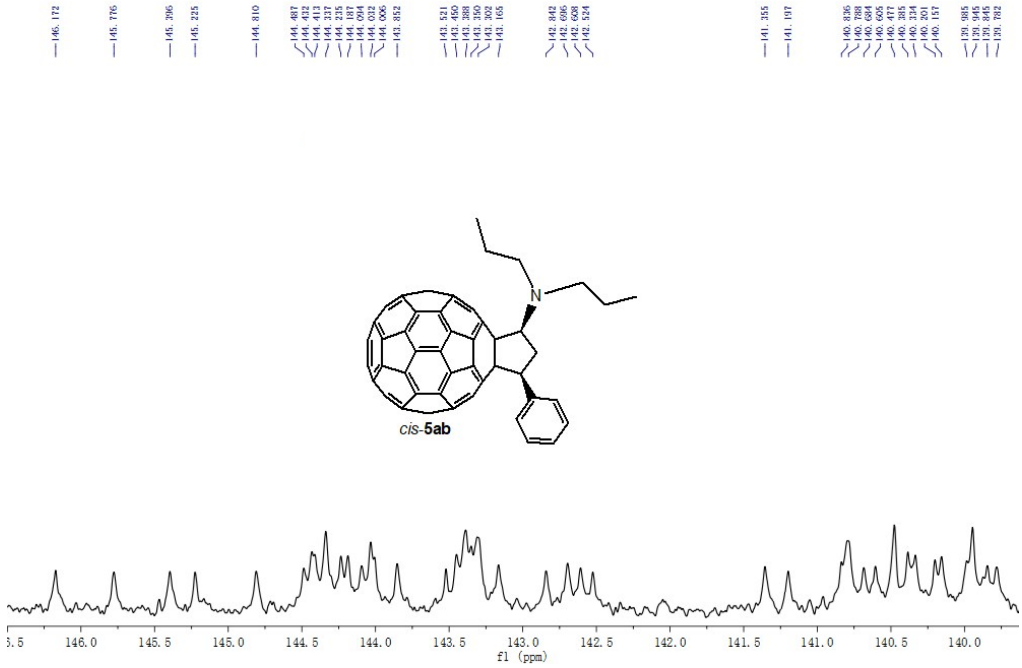


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ab**

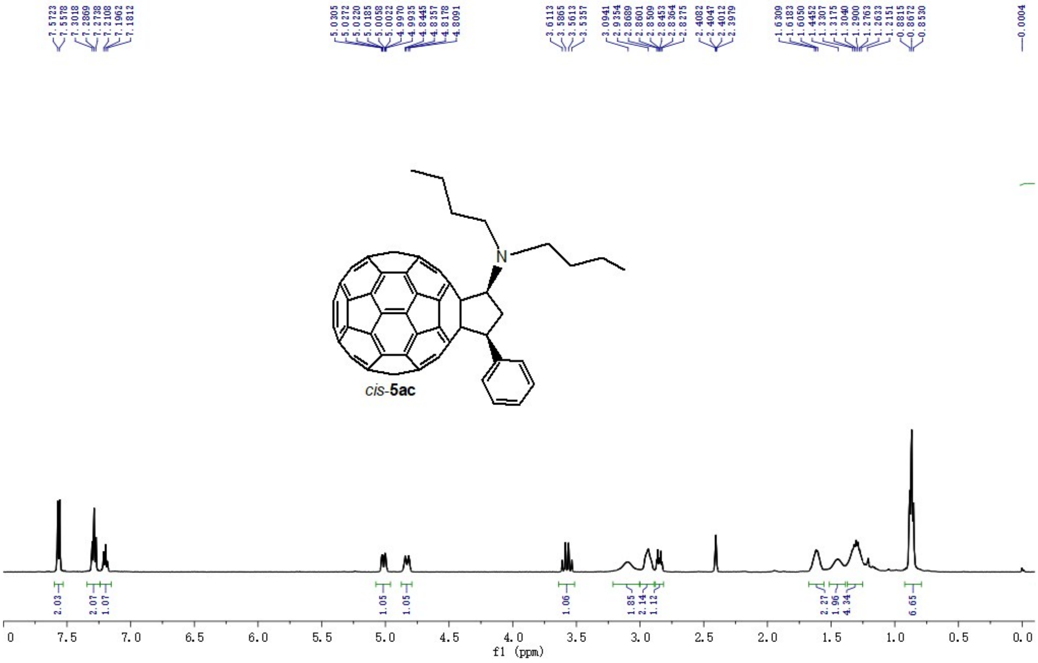


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ab**

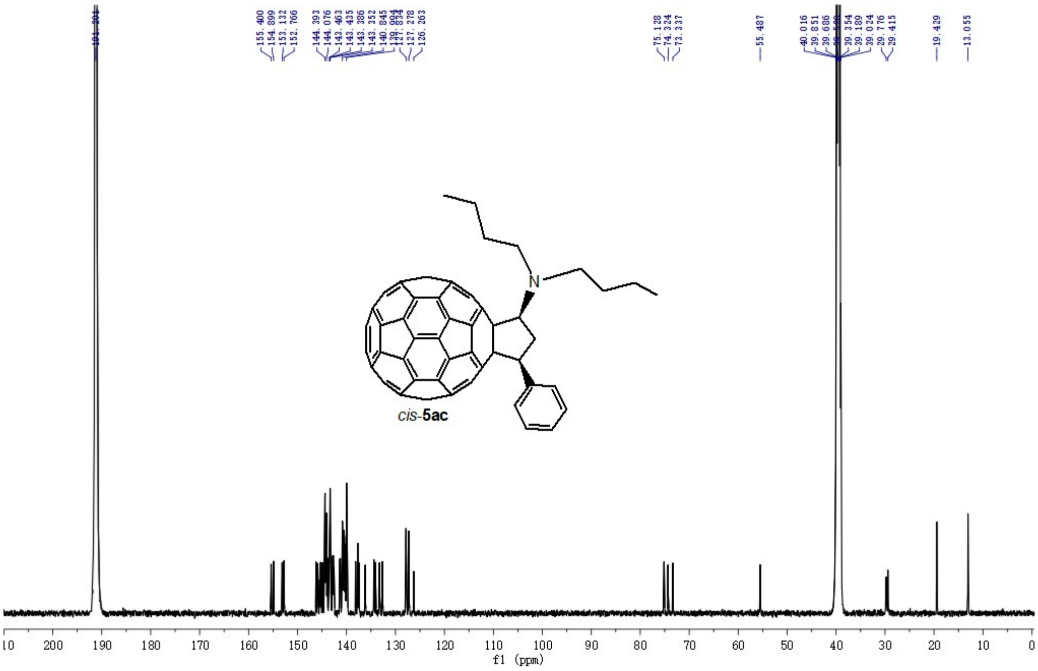


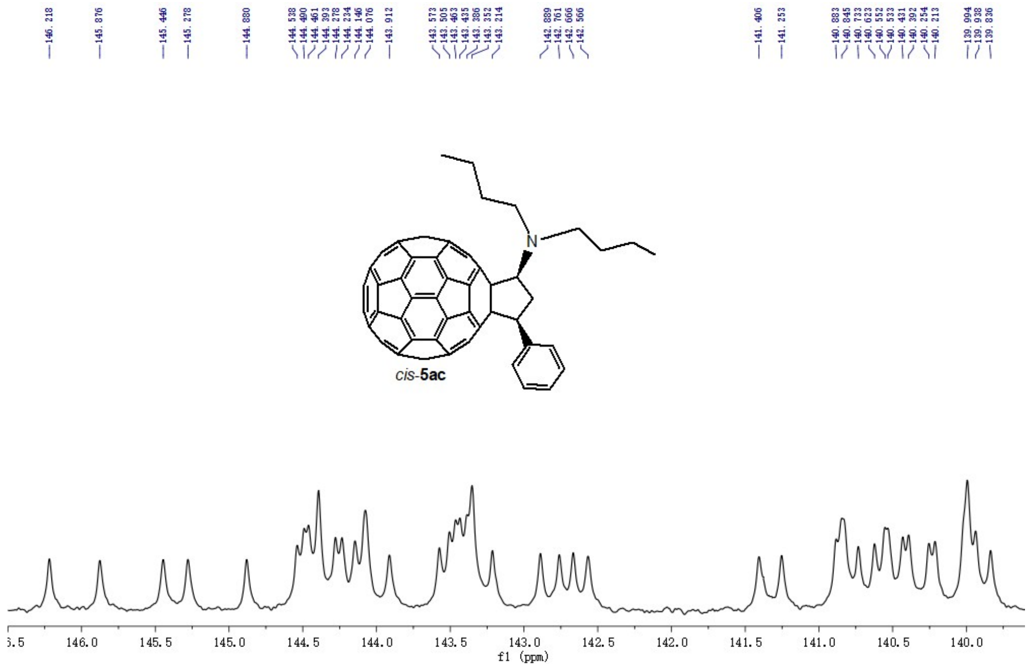


[1]H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ac**

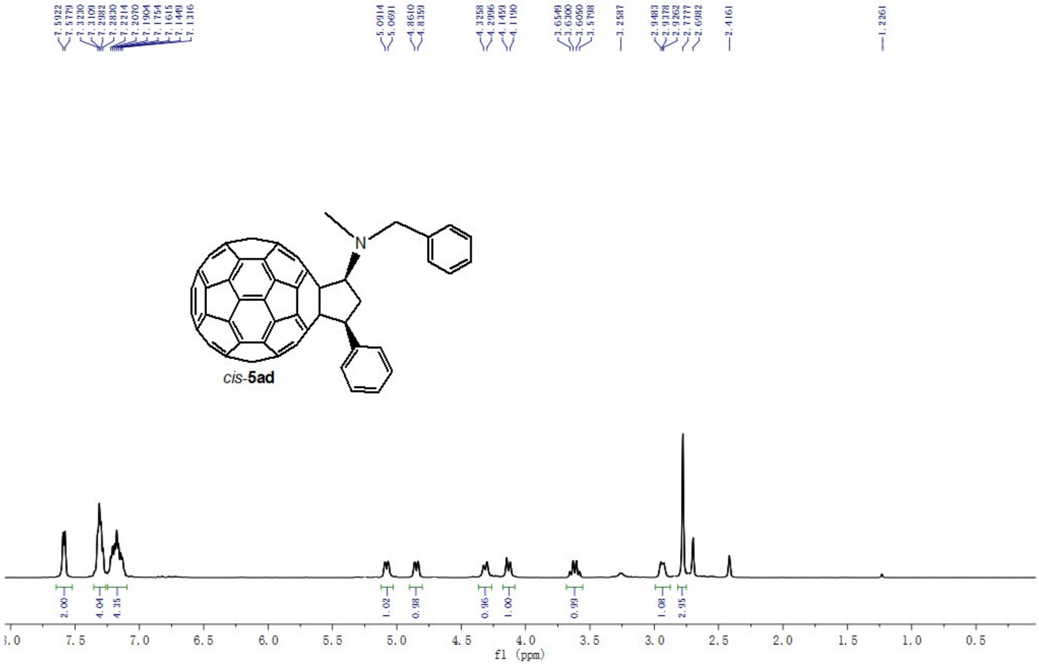


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ac**

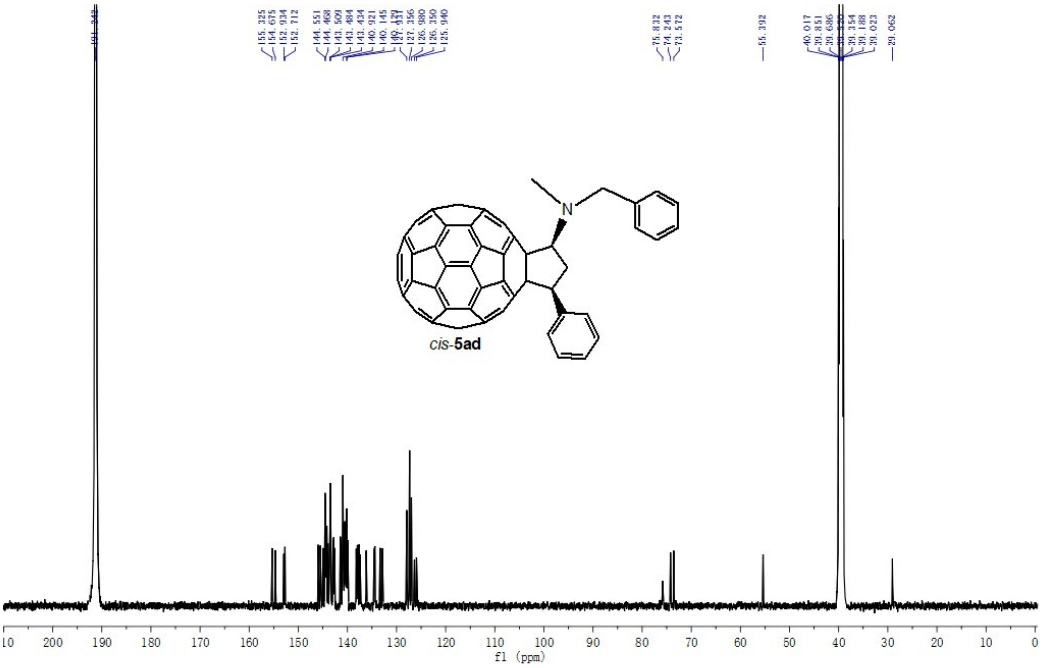


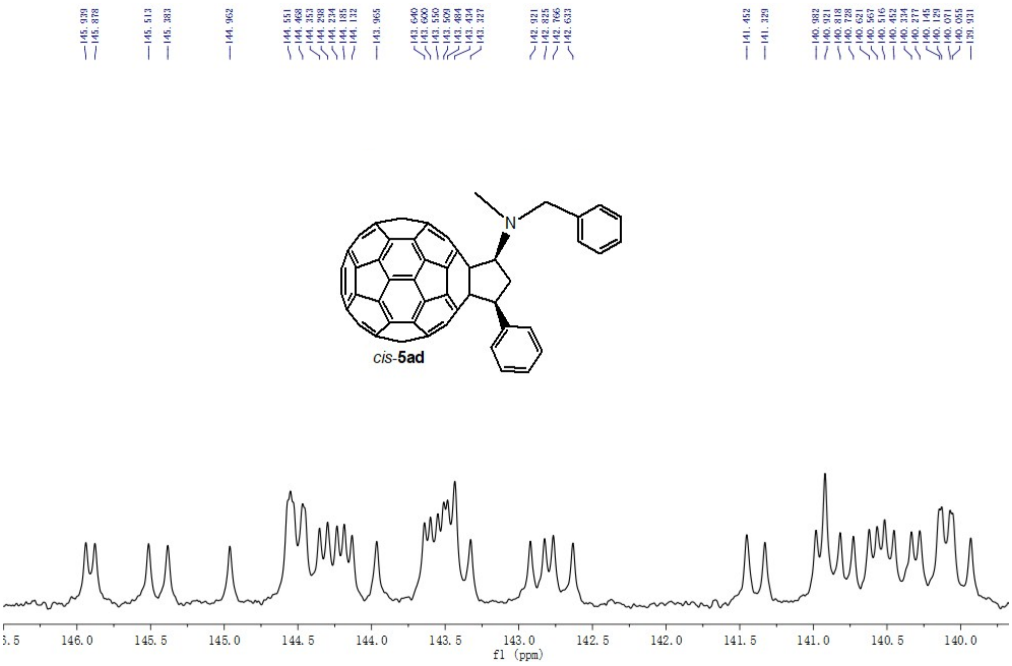


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ad**

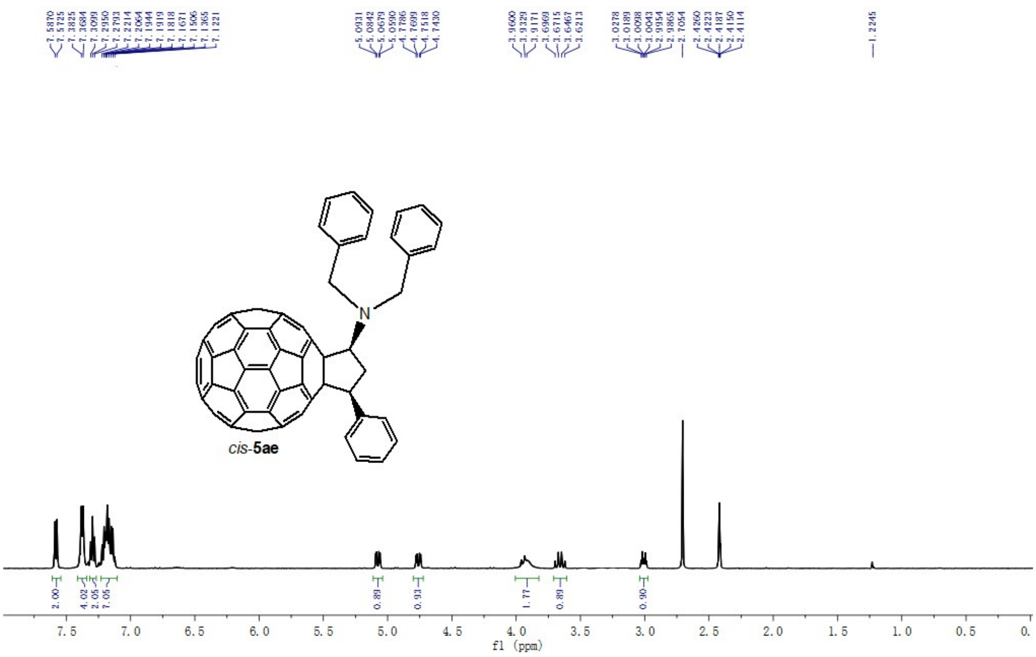


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ad**

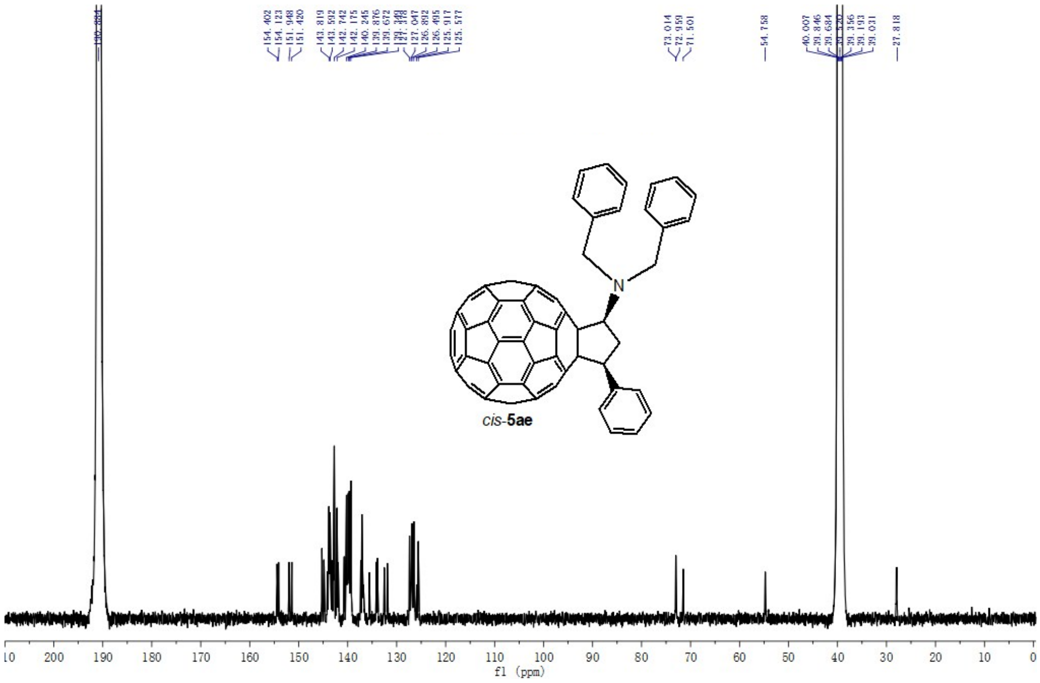


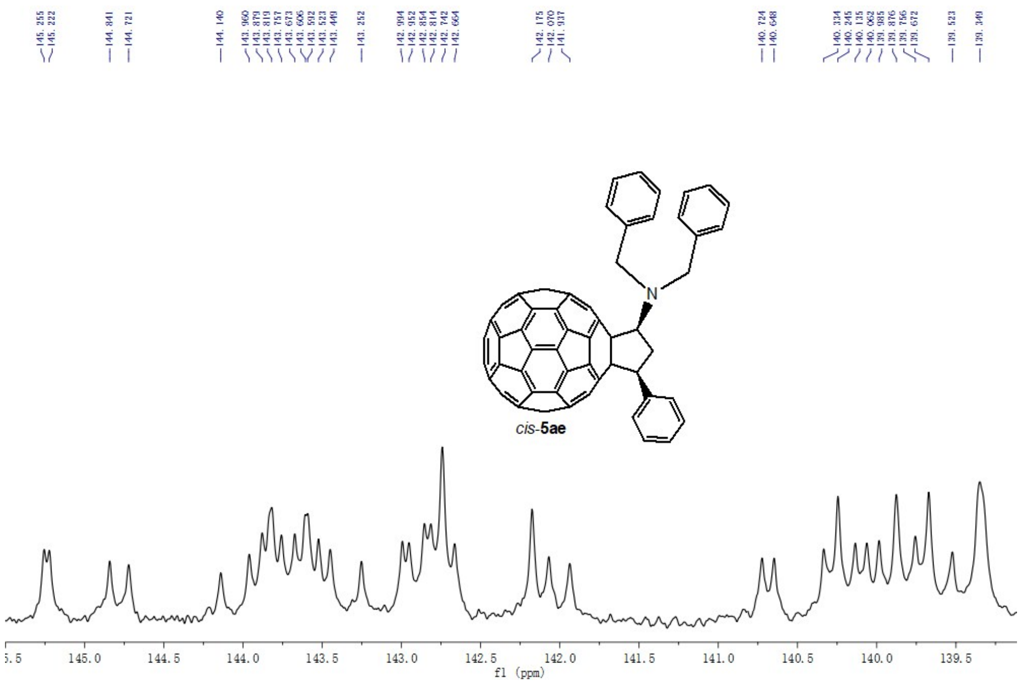


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ae**

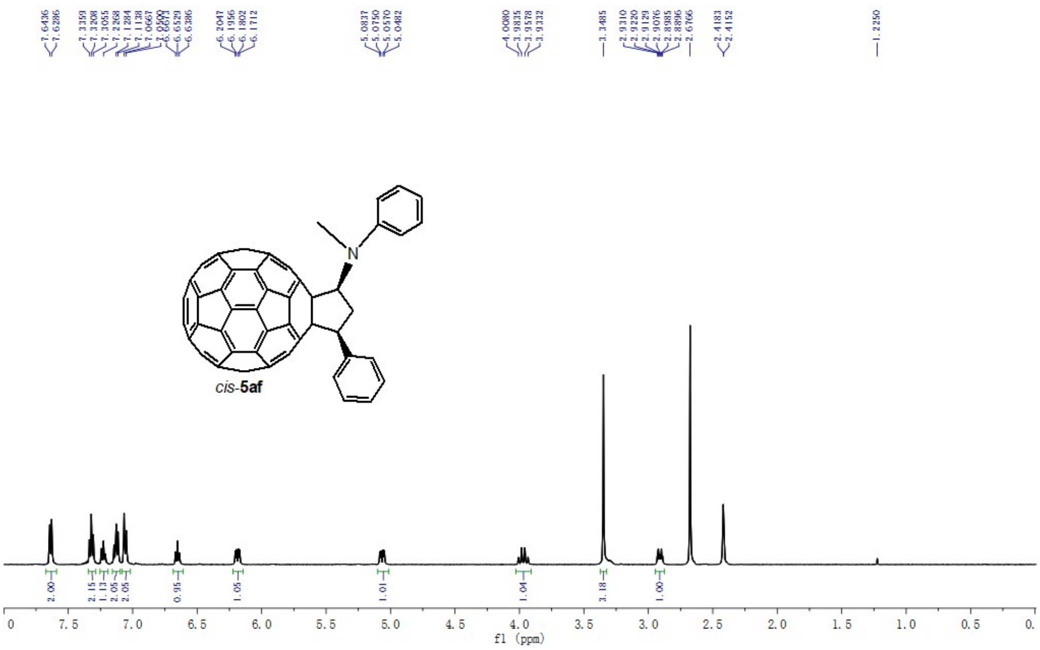


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ae**

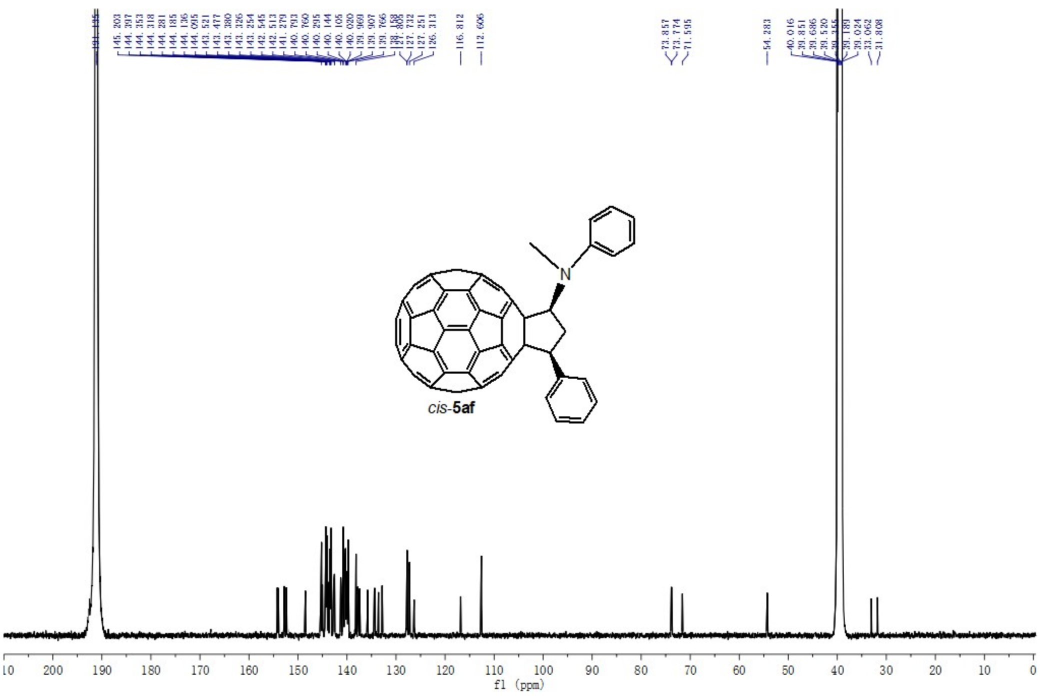


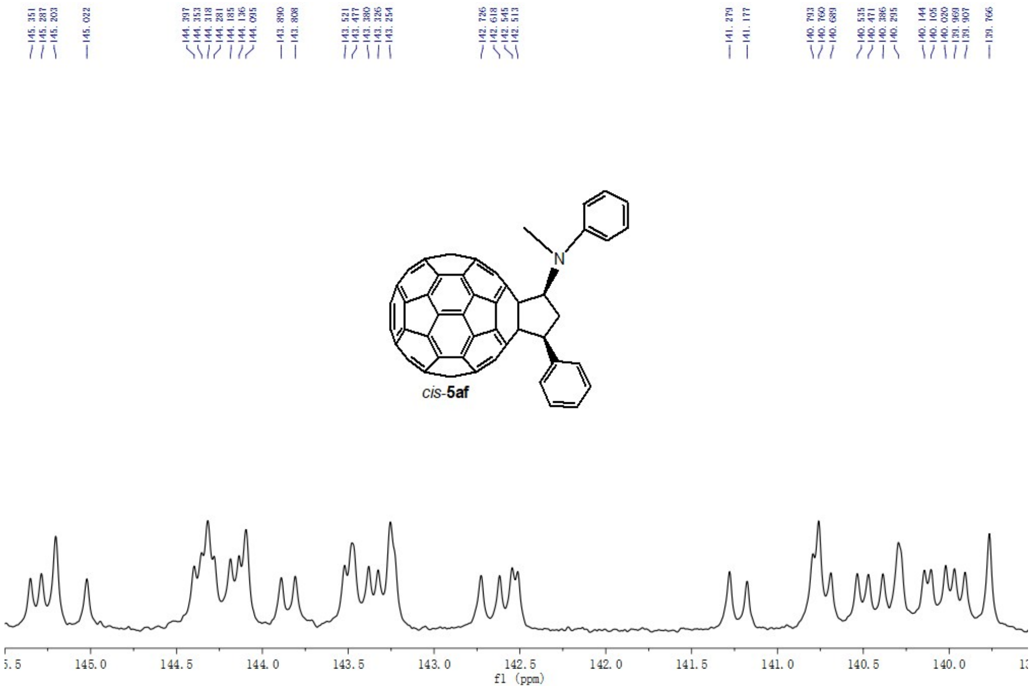


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5af**

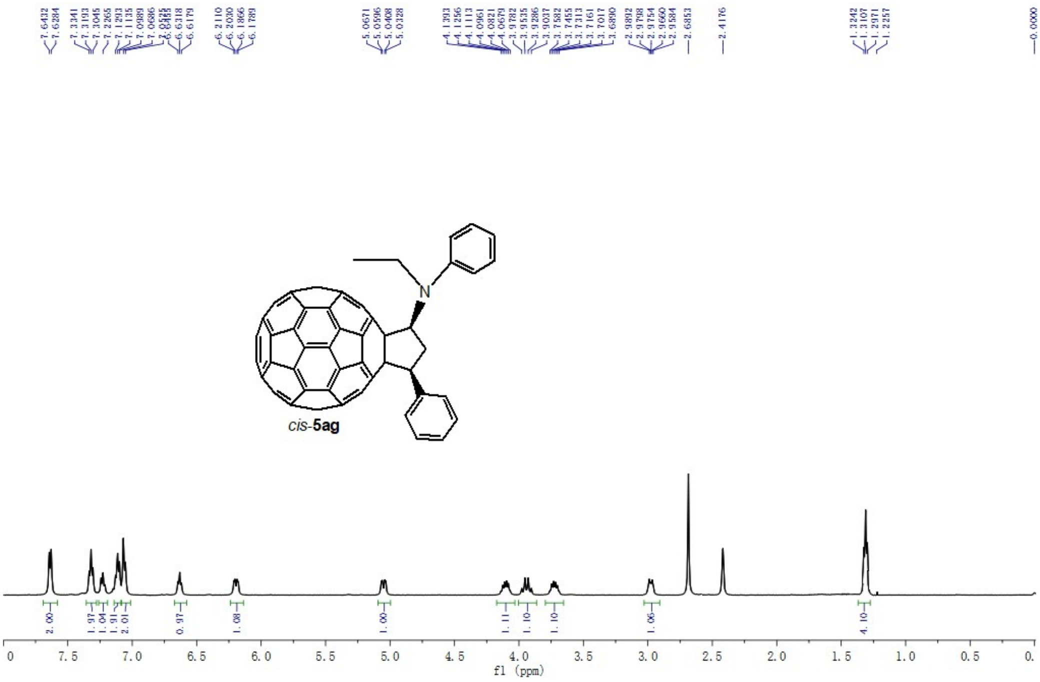


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5af**

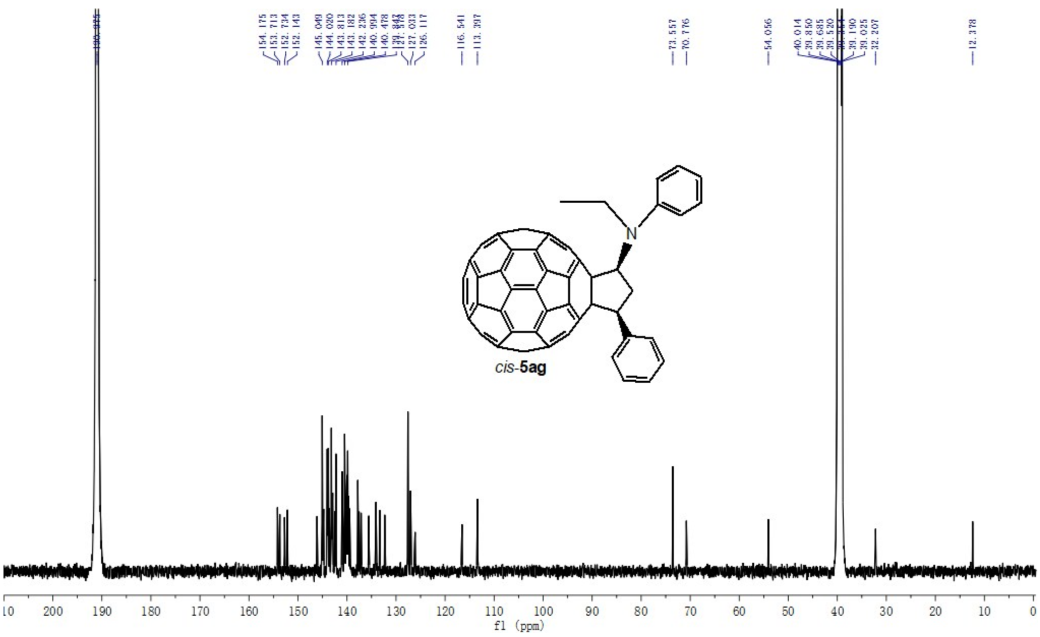


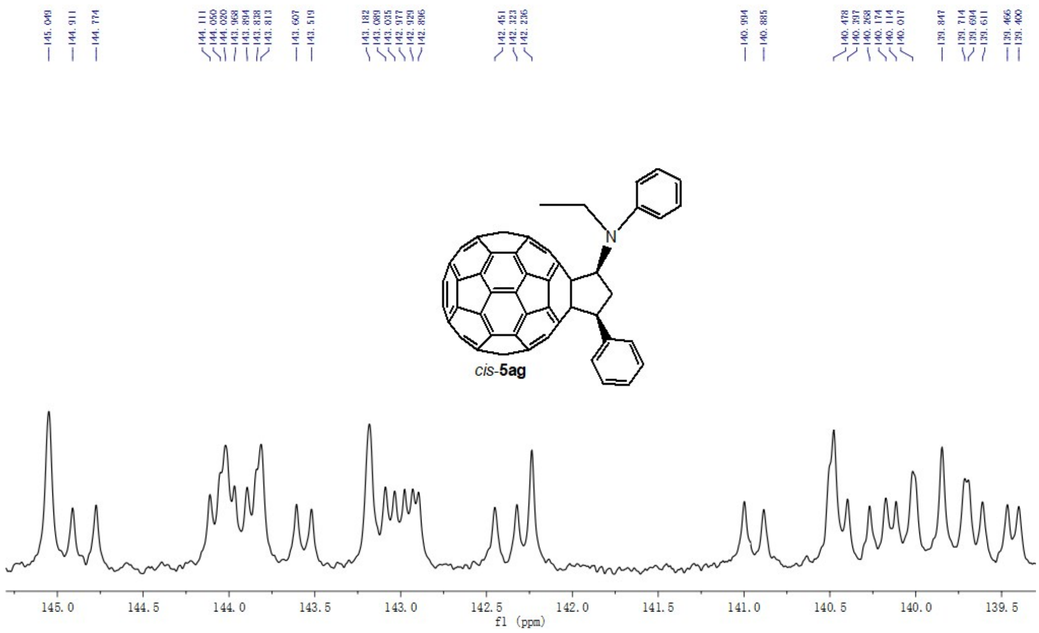


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ag**

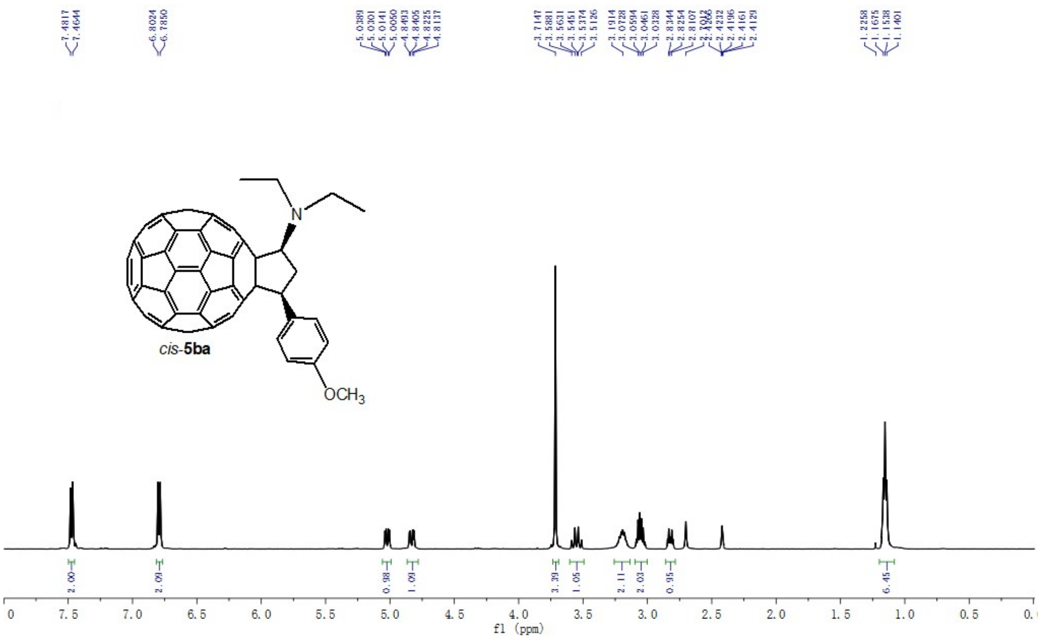


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ag**

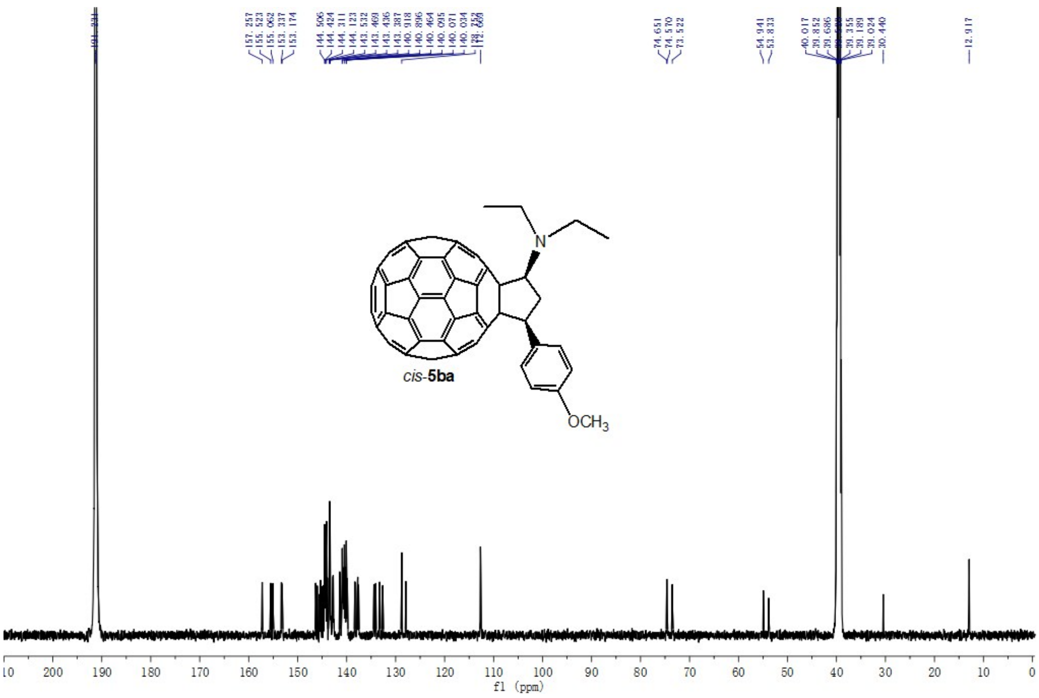


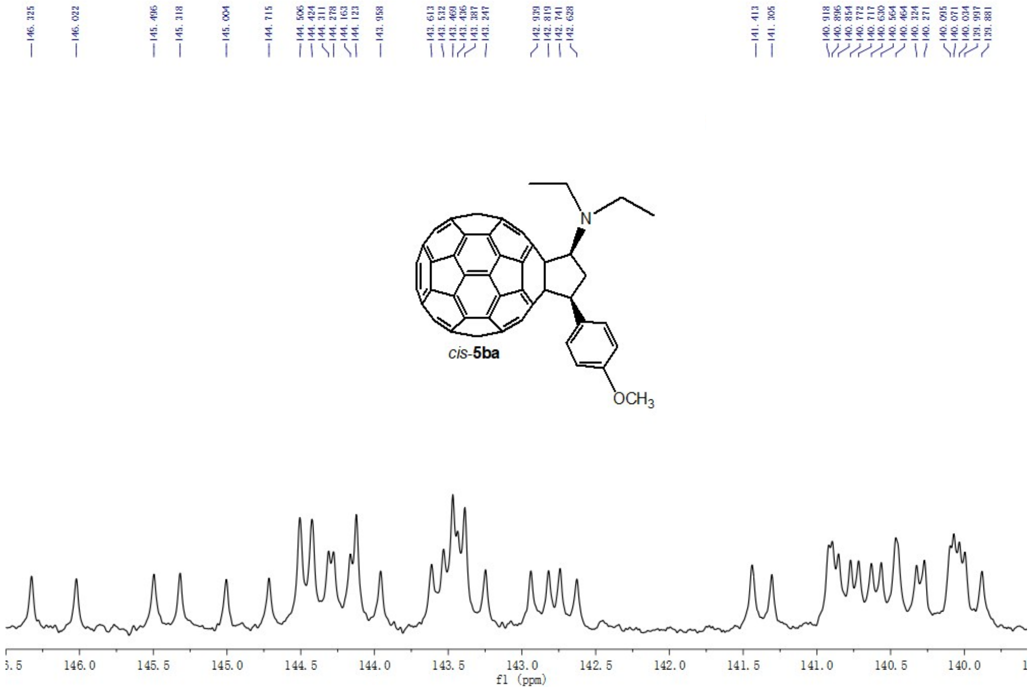


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ba**



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ba**





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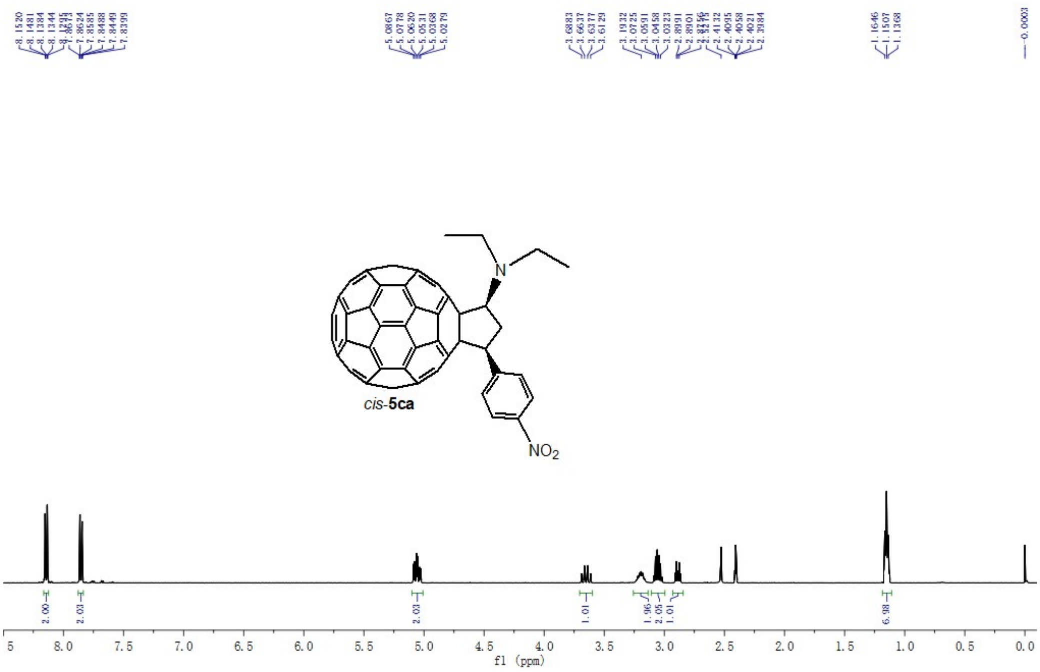
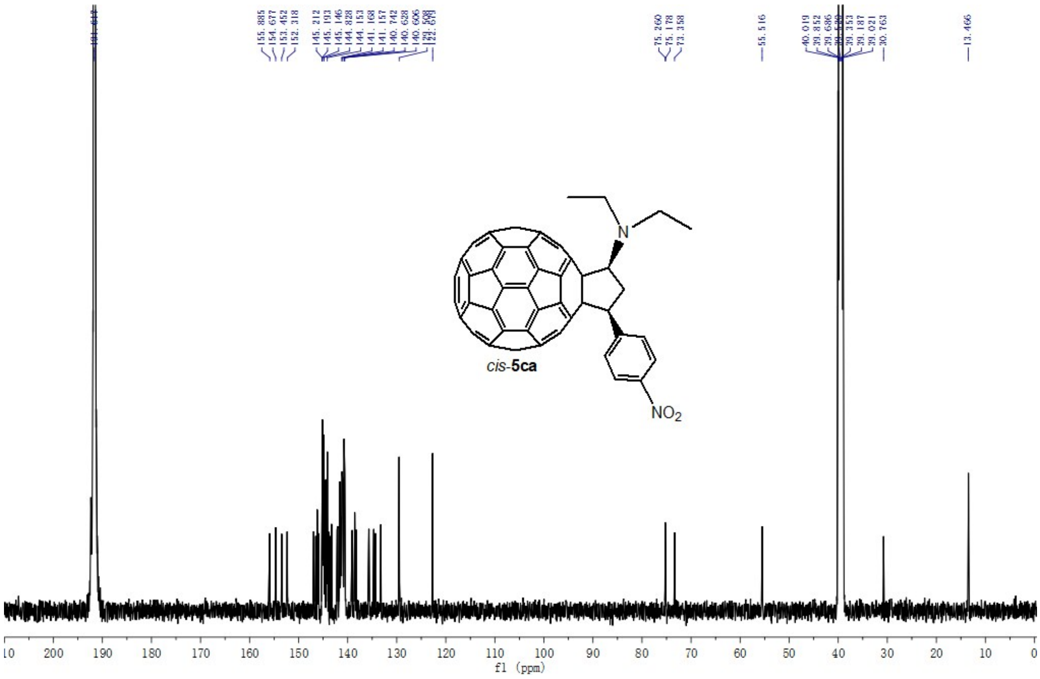
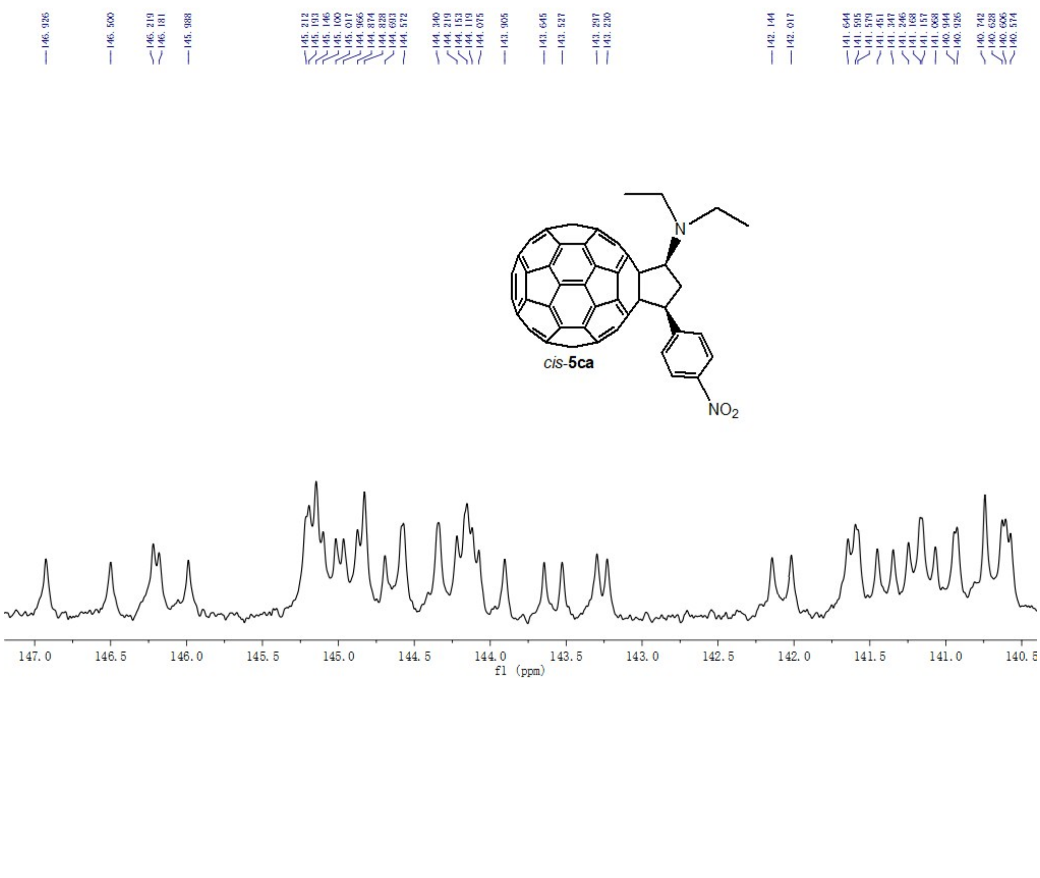
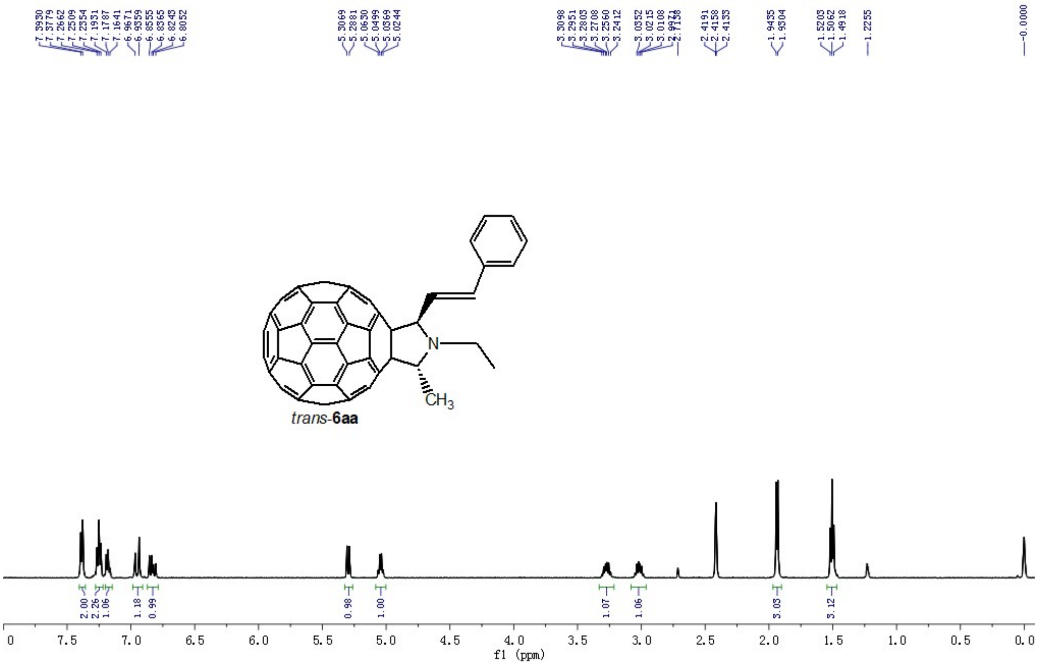


[13]C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**5ca**

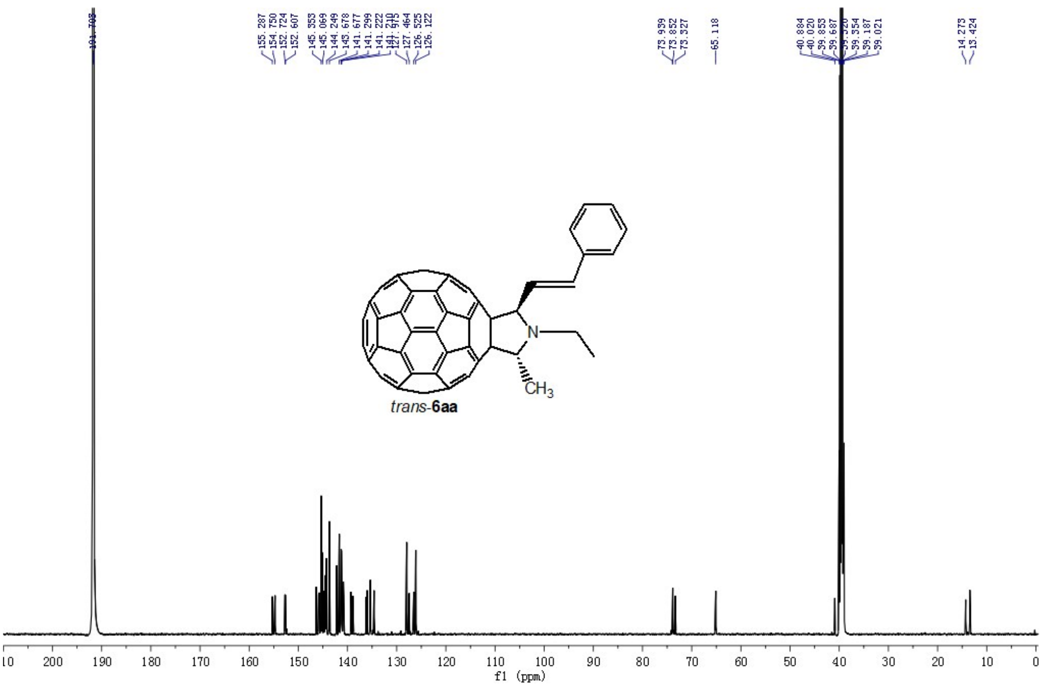


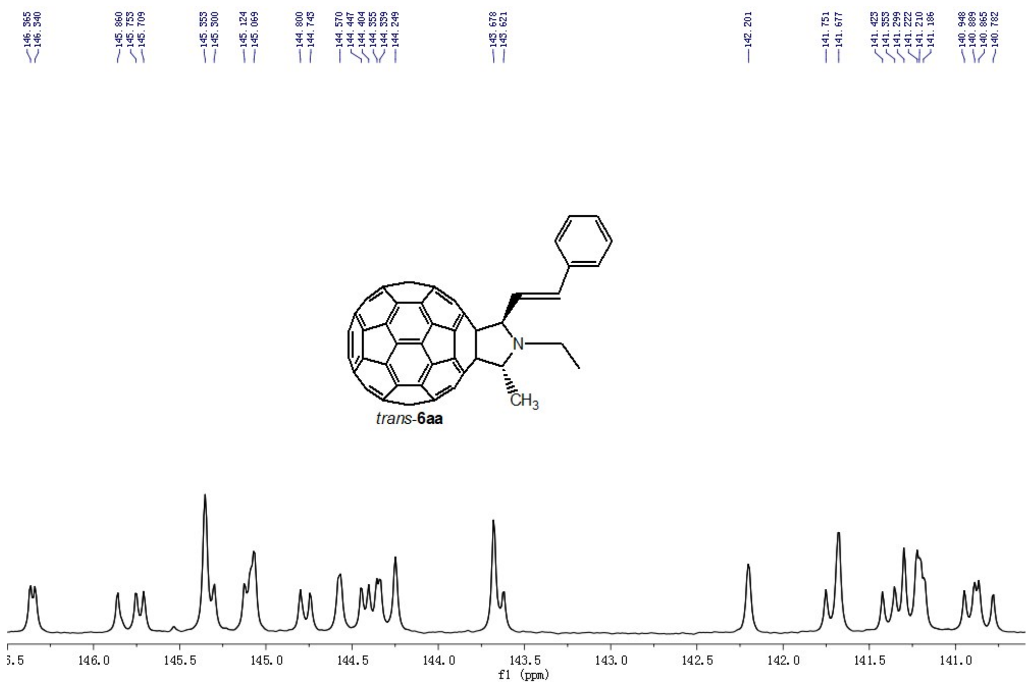


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6aa**

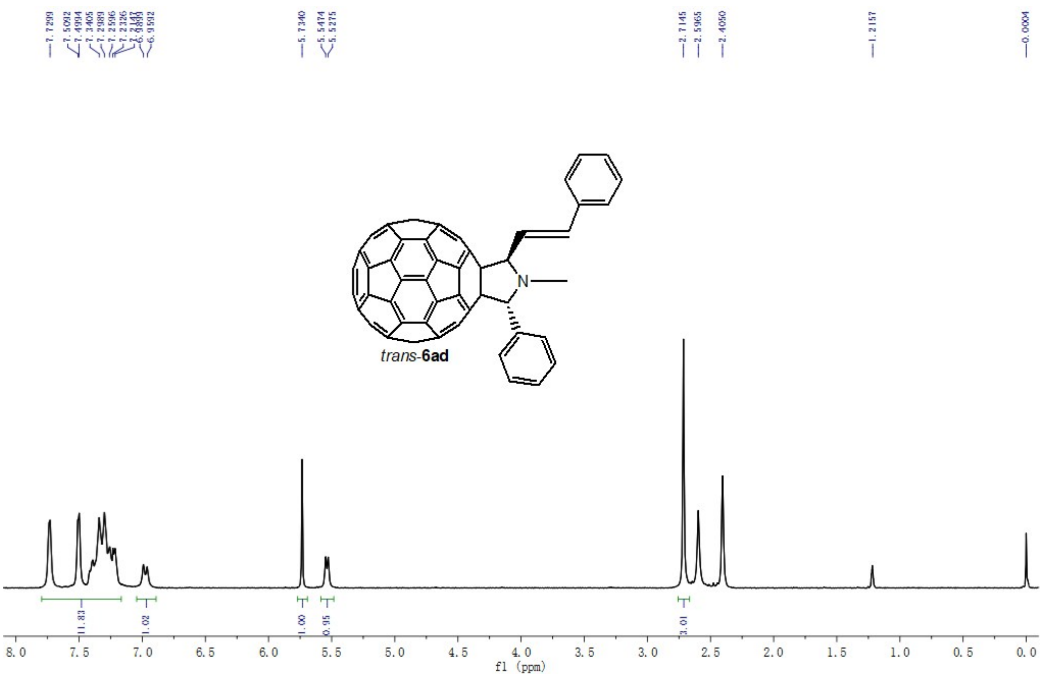


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6aa**

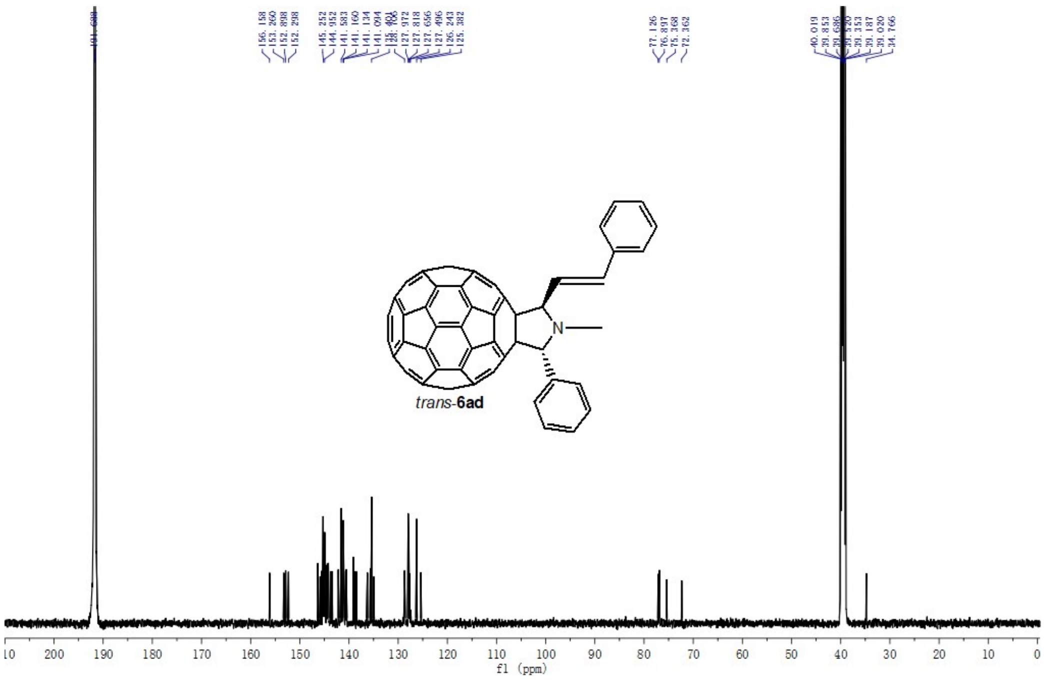


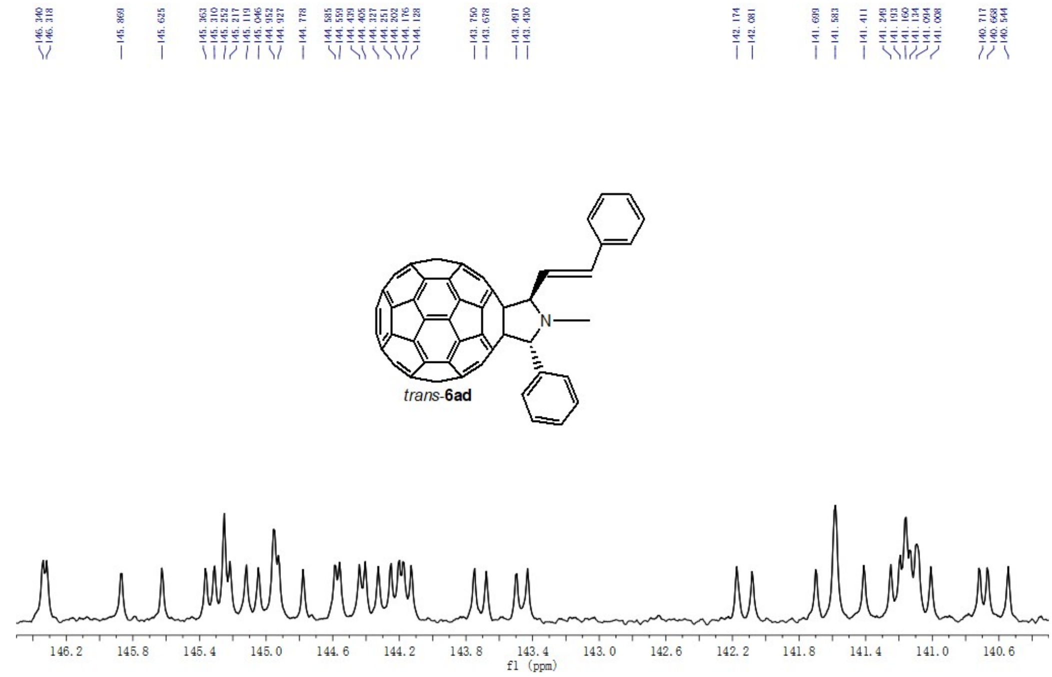


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ad**

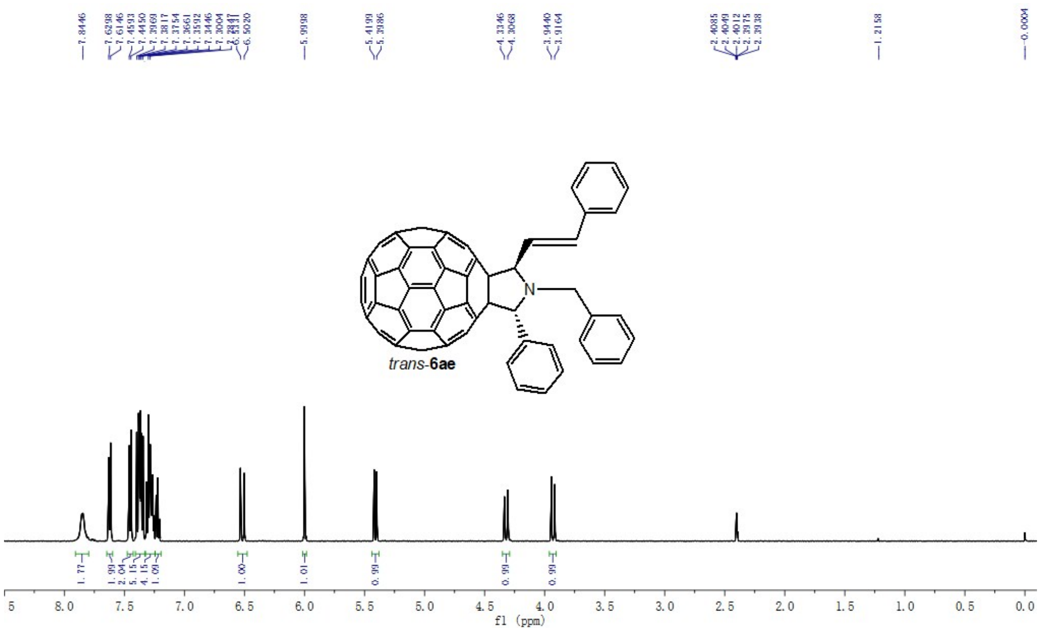


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ad**

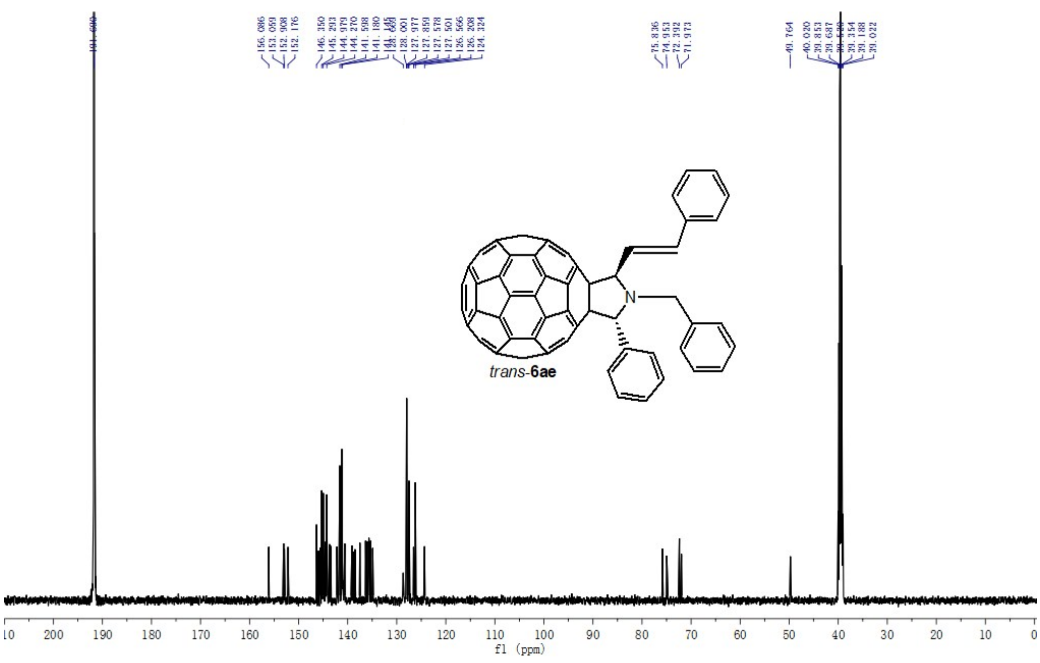


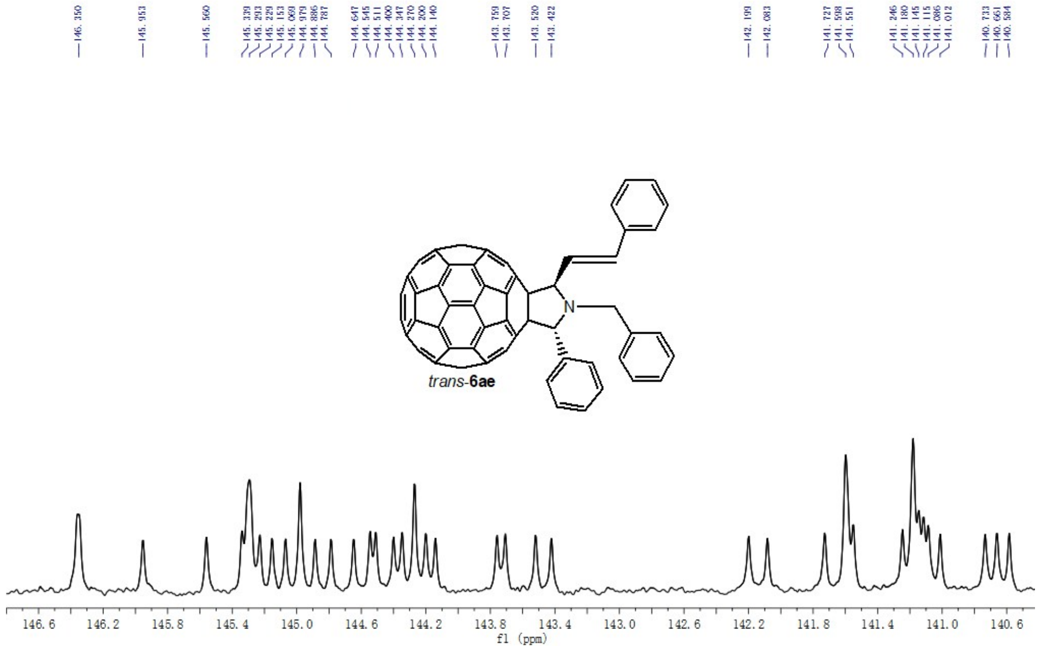


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ae**

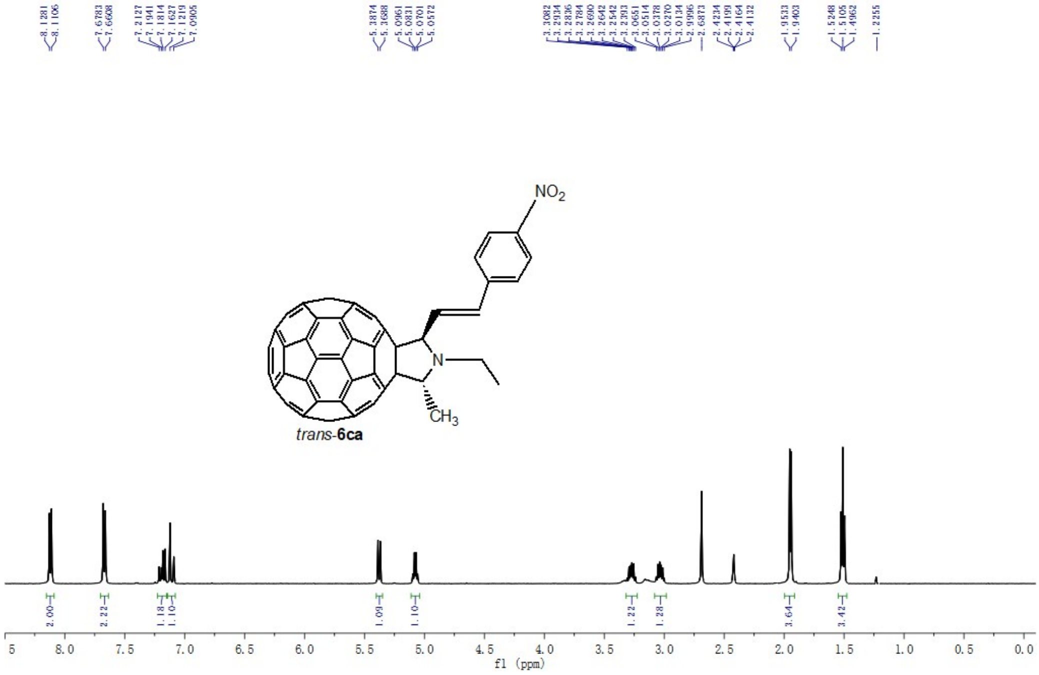


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ae**

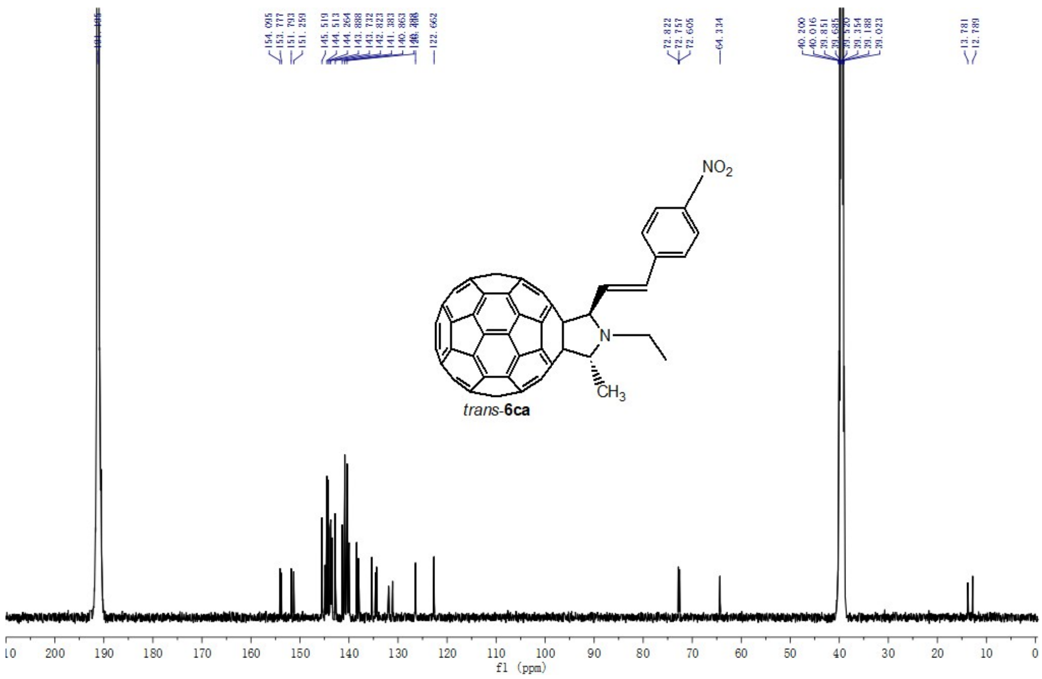


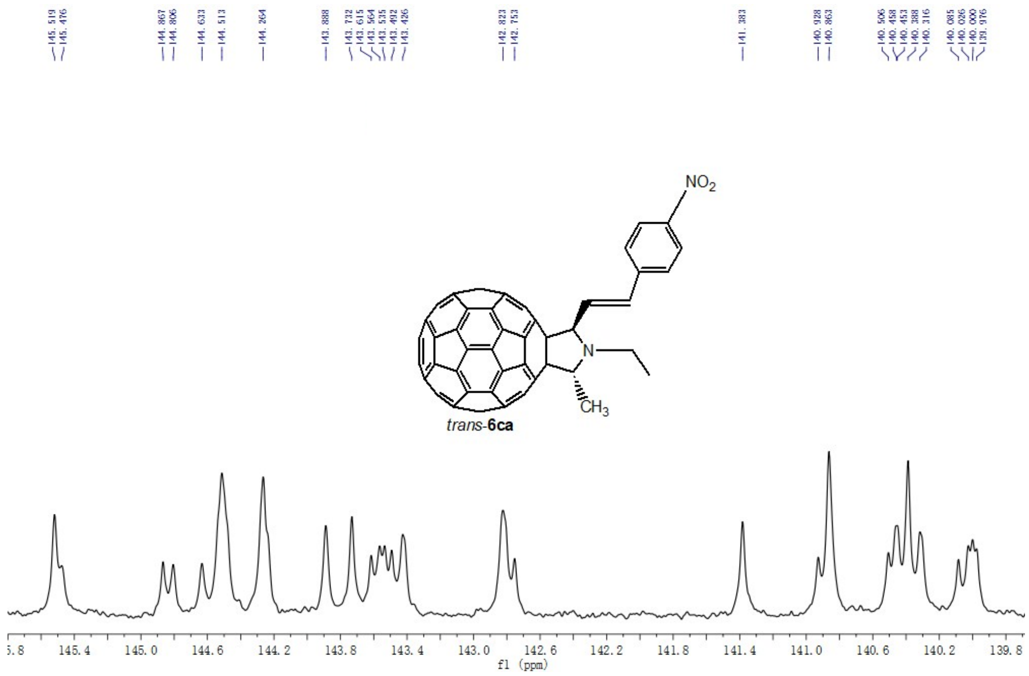


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ca**

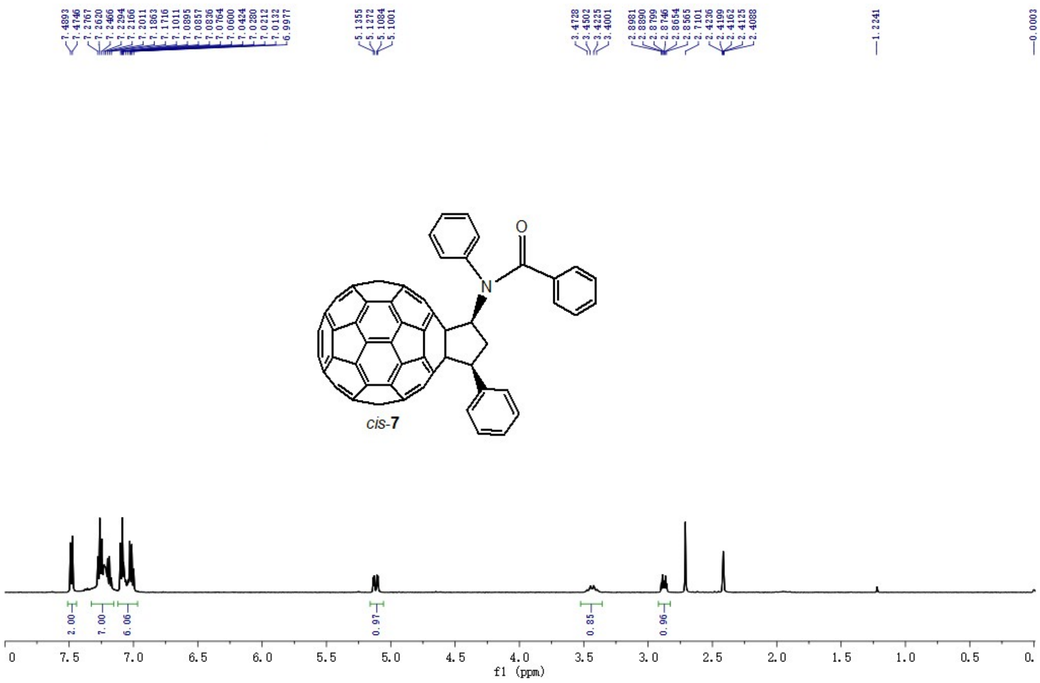


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *trans*-**6ca**

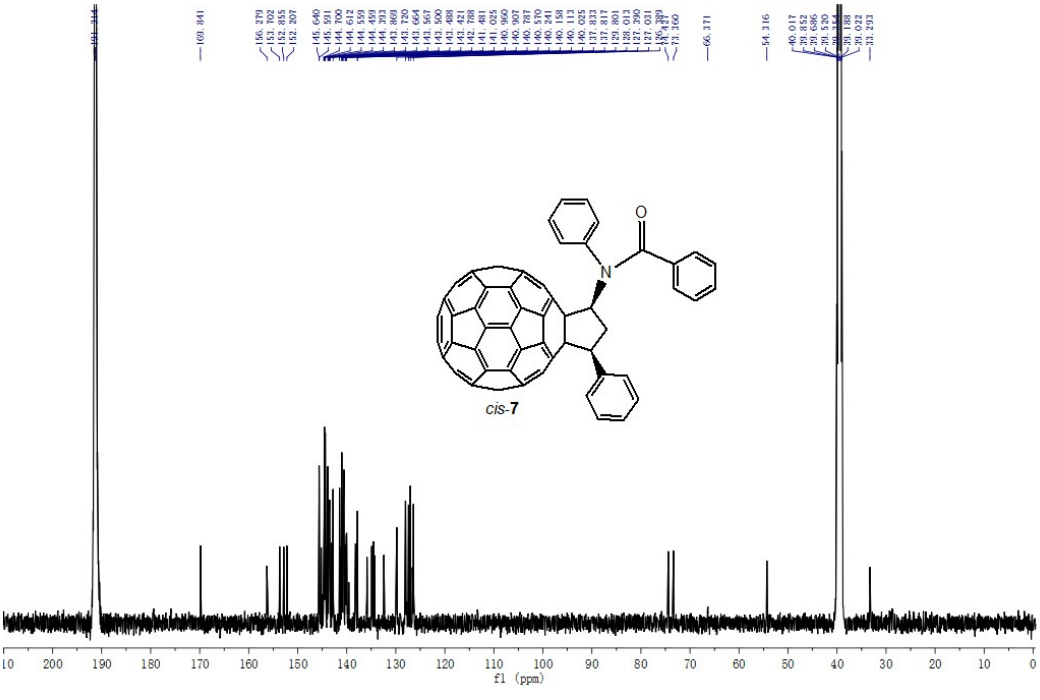


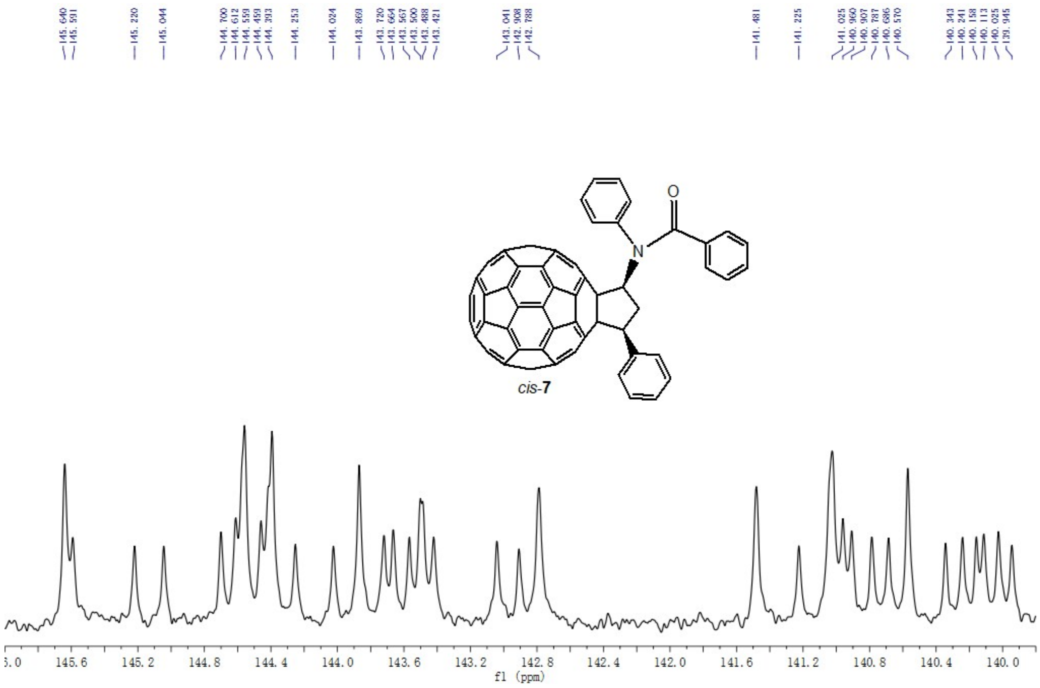


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**7**

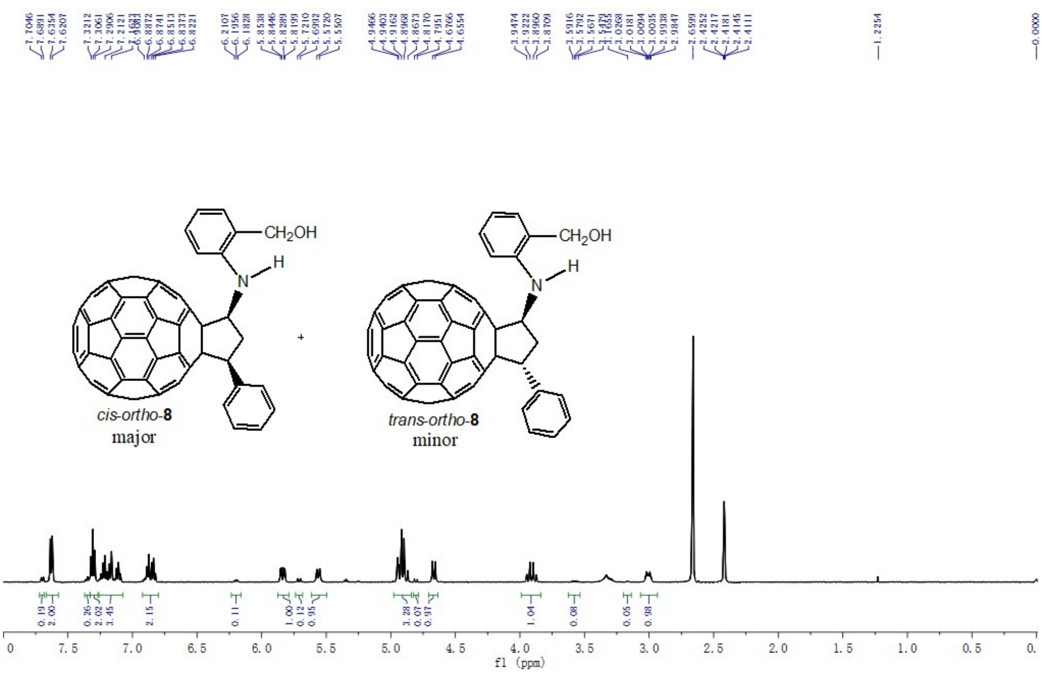


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis*-**7**

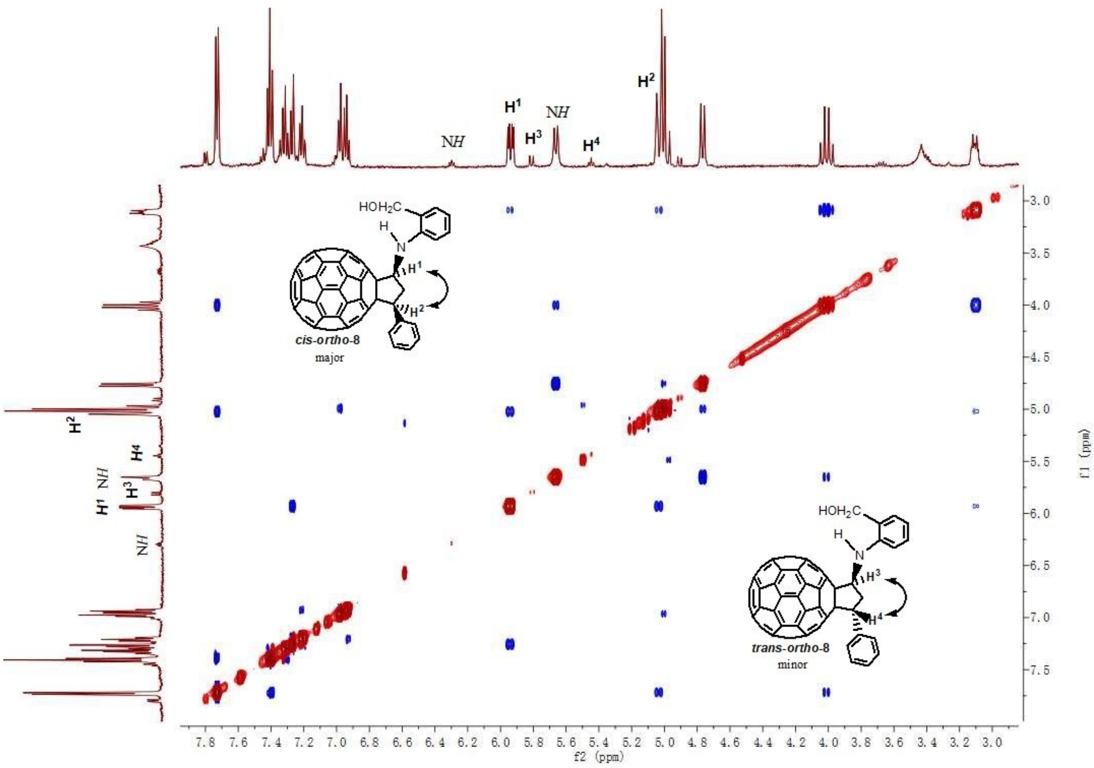




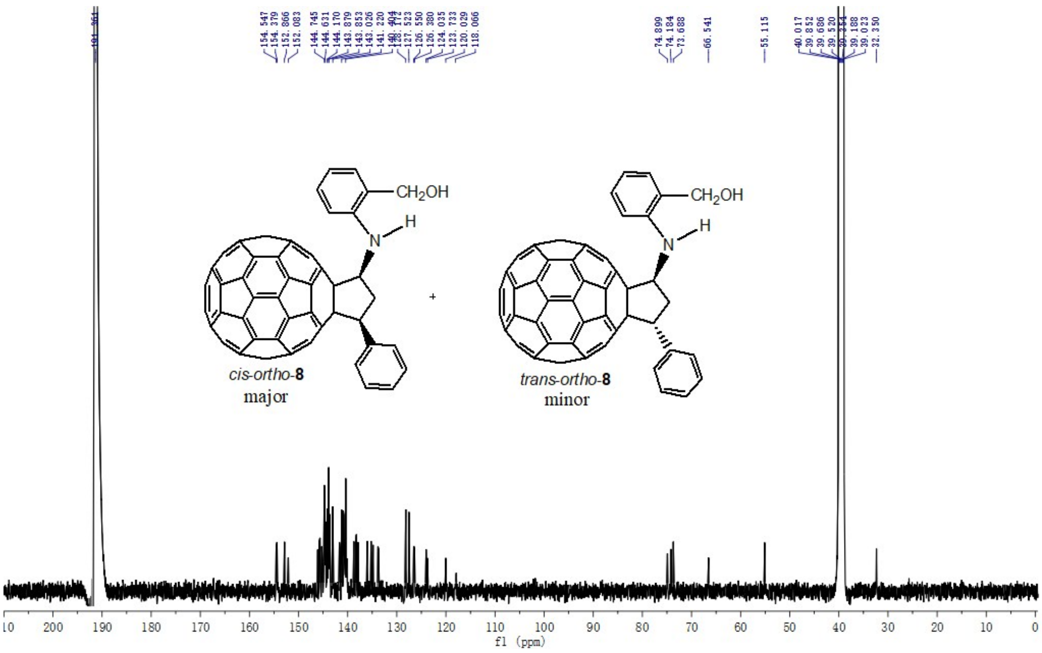
^{1}H NMR (500 MHz, CS_2/DMSO-d_6) spectrum of compound *cis/trans-ortho*-**8**

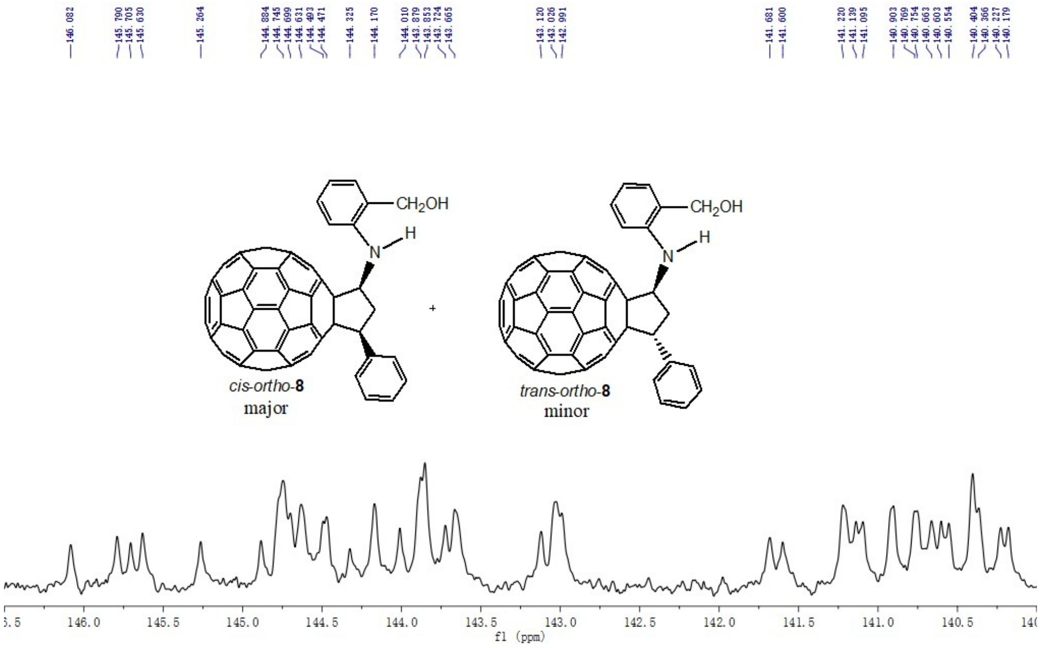


NOESY (500 MHz, CS_2/DMSO-d_6) spectrum of *cis/trans-ortho*-**8**



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) spectrum of compound *cis/trans-ortho*-**8**




CH2OH
H
N
cis-ortho-8
major
+
CH2OH
H
N
trans-ortho-8
minor
f1 (ppm)